Renewable and Sustainable Energy Reviews 15 (2011) 1–23

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Sustainable hydrocarbon fuels by recycling CO_2 and H_2O with renewable or nuclear energy

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ARTICLE INFO

Article history:
Received 23 March 2010
Accepted 14 July 2010

Keywords:
Sustainable fuel
Hydrocarbon fuel
Carbon dioxide recycling
Electrolysis
Energy balance
Economics

ABSTRACT

To improve the sustainability of transportation, a major goal is the replacement of conventional petroleum-based fuels with more sustainable fuels that can be used in the existing infrastructure (fuel distribution and vehicles). While fossil-derived synthetic fuels (e.g. coal derived liquid fuels) and biofuels have received the most attention, similar hydrocarbons can be produced without using fossil fuels or biomass. Using renewable and/or nuclear energy, carbon dioxide and water can be recycled into liquid hydrocarbon fuels in non-biological processes which remove oxygen from CO_2 and H_2O (the reverse of fuel combustion). Capture of CO_2 from the atmosphere would enable a closed-loop carbon-neutral fuel cycle.

This article critically reviews the many possible technological pathways for recycling CO_2 into fuels using renewable or nuclear energy, considering three stages—CO_2 capture, H_2O and CO_2 dissociation, and fuel synthesis. Dissociation methods include thermolysis, thermochemical cycles, electrolysis, and photoelectrolysis of CO_2 and/or H_2O. High temperature co-electrolysis of H_2O and CO_2 makes very efficient use of electricity and heat (near-100% electricity-to-syngas efficiency), provides high reaction rates, and directly produces syngas (CO/H_2 mixture) for use in conventional catalytic fuel synthesis reactors. Capturing CO_2 from the atmosphere using a solid sorbent, electrolyzing H_2O and CO_2 in solid oxide electrolysis cells to yield syngas, and converting the syngas to gasoline or diesel by Fischer–Tropsch synthesis is identified as one of the most promising, feasible routes.

An analysis of the energy balance and economics of this CO_2 recycling process is presented. We estimate that the full system can feasibly operate at 70% electricity-to-liquid fuel efficiency (higher heating value basis) and the price of electricity needed to produce synthetic gasoline at U.S.D$ 2/gal ($ 0.53/L) is 2–3 U.S. cents/kWh. For $ 3/gal ($ 0.78/L) gasoline, electricity at 4–5 cents/kWh is needed. In some regions that have inexpensive renewable electricity, such as Iceland, fuel production may already be economical. The dominant costs of the process are the electricity cost and the capital cost of the electrolyzer, and this capital cost is significantly increased when operating intermittently (on renewable power sources such as solar and wind). The potential of this CO_2 recycling process is assessed, in terms of what technological progress is needed to achieve large-scale, economically competitive production of sustainable fuels by this method.

Contents

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1364-0321/$ – see front matter
doi:10.1016/j.rser.2010.07.014

1. Introduction

Hydrocarbon fuels provide the majority of all transportation energy, and petroleum is the dominant feedstock from which transportation fuels are produced. Hydrocarbons[1] produced from other feedstocks (fossil and biomass), as well as carbon-free energy carriers (such as hydrogen, batteries and ultracapacitors), are potentially more sustainable alternatives. The benefits of hydrocarbons over carbon-free energy carriers include higher energy density and use of existing infrastructure (fuel distribution and vehicles). While increased use of electric propulsion will likely reduce liquid fuel demand, hydrocarbons will continue to be needed—especially as fuels in aircraft, sea vessels, and haulage vehicles, and they also provide the chemical building blocks for much of the chemical industry. Their widespread use calls for means to produce them sustainably.

As a direct replacement for petroleum-based hydrocarbons, biofuels and fossil carbon derived synthetic fuels (e.g. coal derived liquid fuels) are receiving the most attention. Their sustainability depends largely on the source of the feedstock and, in the case of fossil carbon based fuels, on the availability of carbon capture and storage technologies and sites. Similar hydrocarbons can also be produced without using fossil fuels or biomass. Using renewable and/or nuclear energy (in the form of heat, electricity, and/or sunlight), carbon dioxide and water can be recycled into hydrocarbon fuels (Fig. 1) in a non-biological process. Initially, CO_2 captured from large industrial sources (e.g. aluminum plants) could be utilized. In the long term, the capture of CO_2 from the atmosphere [1] would enable a closed-loop hydrocarbon fuel cycle (Fig. 1).

When solar energy drives the dissociation of CO_2 and H_2O, the fuel cycle is comparable to that of biofuels: synthetic "trees" collect CO_2 from the air and use solar energy to fix it as carbon (Fig. 2). However, this fuel cycle avoids the biomass intermediate product, which consumes a lot of resources to cultivate (water, fertilizer, etc) and needs to be processed further to produce a fuel. Far less land would be needed for photovoltaic or solar thermally driven fuel production than for land-based biofuel production; even with low-efficiency solar panels driving the process, the components would cover less than a tenth of the land area that is needed to grow typical biomass used for energy.[2] The land also needs neither to be fertile nor artificially fertilized, avoiding competition with food agriculture and other important land uses. In fact, as will be discussed later, one potentially optimal location for this process is the desert. A remote, sunny desert site could provide the inexpensive solar electricity and/or heat to run the process, and the system could be built right at that site. Algae-based biofuels share some of these same advantages over land-based biofuels.

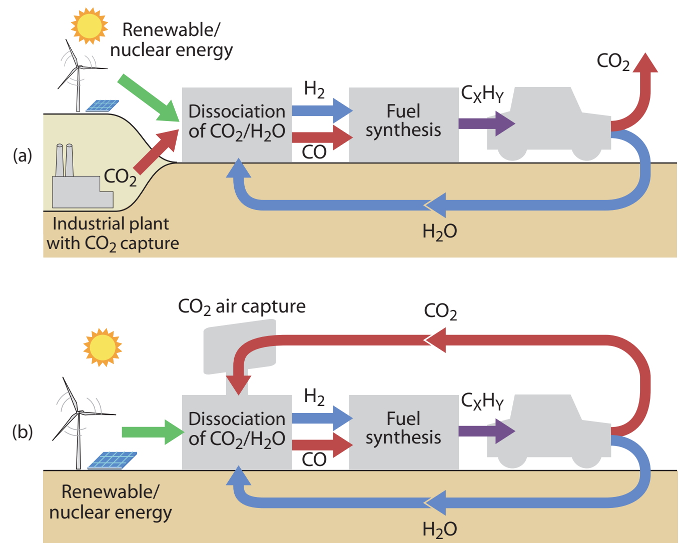


Fig. 1. CO_2-recycled synthetic fuel cycles. (a) Once-through re-use of CO_2, resulting in net CO_2 emissions of approximately 1/2 versus the emissions that would occur without any re-use (both from the industrial plant and from transportation), (b) continuous closed-loop carbon recycling via air capture of CO_2, resulting in near zero net emissions. These approximations neglect life-cycle emissions of energy generation, CO_2 capture, materials, construction, etc. C_XH_Y represents hydrocarbon fuel.

Still, like all biomass, aquatic biomass is optimized to support the life processes of the living organism, not to produce fuel. Further, living organisms are vulnerable to performance loss due to changes in environmental conditions or interaction with other living organisms. Even with genetic engineering it seems unlikely that an organism can be created that matches the efficiency, robustness, and economy that can be achieved by a more direct energy conversion.

In comparison with hydrogen as a fuel, CO_2-recycled fuels are a form of chemical storage of hydrogen alongside carbon. Production of such fuels would be similar to hydrogen production (and likely even involve the production of H_2 by H_2O dissociation) while distribution and consumption would be similar to that of other hydrocarbons (Fig. 2). Fuel production can use a variety of sustainable resources, and the fuel is distributed and consumed using the existing hydrocarbon fuel based infrastructure and vehicles. The difficulties of a large-scale hydrogen-only fuel cycle – the significant efforts needed to store and distribute the highly volatile gas and to build an entirely new infrastructure – are avoided.

Recycling CO_2 into a hydrocarbon fuel would open a new sector, the transportation fuel sector, to renewable energy, which was previously not accessible to renewable energy sources apart from biomass. Because liquid transportation fuels are a high value form of energy, CO_2 recycling using renewable energy could facilitate growth of renewable energy sources by providing a potentially economical way of delivering renewable energy to the consumer. Synthetic fuel production using intermittent renewable electricity advantageously provides a large time-flexible demand for renew-

[1] "Hydrocarbons" will be used throughout this article to refer to a range of carbonaceous fuels, including gasoline, diesel, alcohols, dimethyl ether, etc.

[2] Typical biomass captures less than 1% of solar energy, and further energy losses in conversion of biomass to fuel result in a fuel ethanol efficiency from solar energy, using corn and sugarcane feedstocks, of around 0.16–0.24% [2]. Commercial solar panels convert around 10–30% of sunlight to electricity, and fuel production from electricity can be accomplished with around 70% efficiency, as will be seen later in this article.

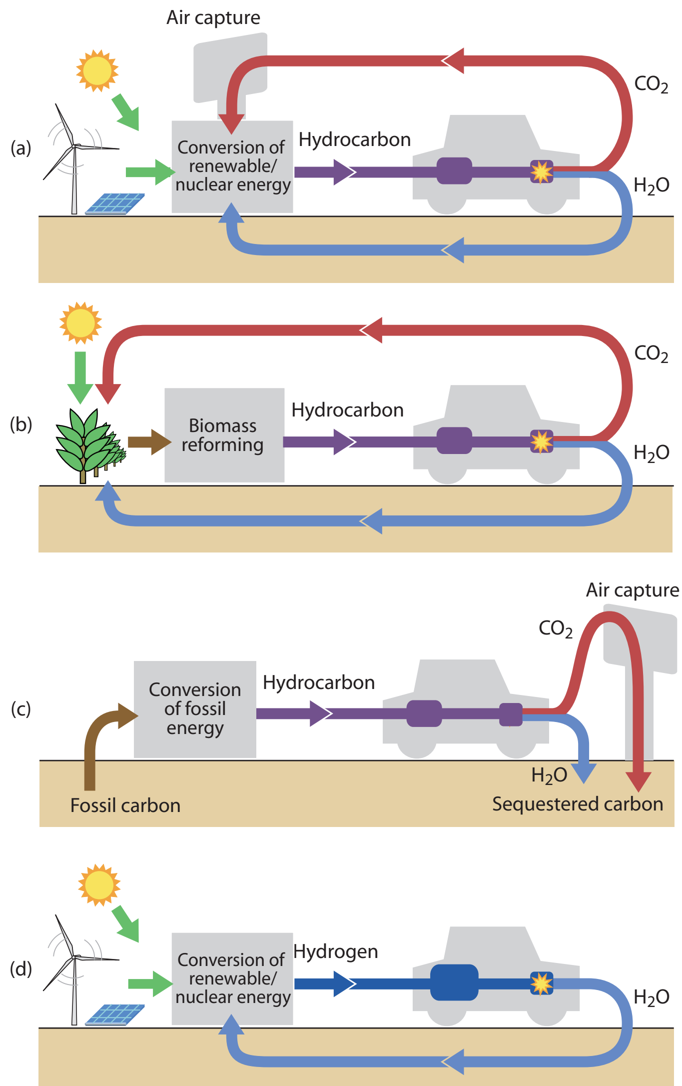


Fig. 2. Comparison of carbon-neutral fuel cycles for hydrocarbons produced using (a) renewable/nuclear energy (shown as solar and wind energy), (b) biomass, (c) fossil fuel. (d) Hydrogen produced by solar/wind energy is also shown for comparison with (a). Whereas the renewable energy based cycles (a, b, and d) are considered materially closed, the fossil fuel based cycle (b) is carbon-neutral but the carbon is stored in an oxidized form.

able electricity; synthetic fuels can be made preferentially when excess electricity supply is available, reducing the demand for energy storage systems that are designed to accept and return electric power (e.g. pumped hydro storage, compressed air storage, batteries, etc.).

The fuel cycles of carbon-neutral hydrocarbons from various sources, alongside a hydrogen fuel cycle, are illustrated in Fig. 2. A more thorough analysis of the sustainability of various energy carriers, including CO_2-recycled synthetic fuels, is a topic of future work.

This article examines the possible electrochemical, thermochemical, and photochemical pathways to produce CO_2-recycled synthetic fuels, and it reviews the current status of the enabling technologies at each stage of the pathway (CO_2 capture, H_2O/CO_2 dissociation, and fuel synthesis). This review mainly focuses on the dissociation stage, where the major energy conversion takes place. High temperature electrolysis of H_2O and/or CO_2 in a solid oxide cell to yield CO and H_2 (syngas) followed by catalytic fuel synthesis is identified as one of the most promising routes. The technical and economic details of this particular process are then examined and the potential of the process is assessed, in terms of what technological progress is needed to make implementation feasible and the circumstances (physical location of deployment and energy market conditions) that would enable affordable implementation.

2. CO_2-recycled synthetic fuel pathways

The synthetic fuel production process has several stages: (1) collection of energy, (2) collection of the oxides, H_2O and CO_2, (3) dissociation of the oxides, and (4) fuel synthesis from the products of stage 3. Within each stage, there are a number of technology options. Fig. 3 presents a map of the possible pathways from the feedstocks to hydrocarbon fuels. Except for direct sunlight-driven processes, the energy collection stage can be considered external to the process; other pathways are not tied to a specific energy source but rather to intermediate heat or electricity. The energy can drive the dissociation of either CO_2 or H_2O, or both, resulting in energy-rich gas mixtures which are readily converted to convenient fuels. Shown in Fig. 1 is the production of syngas (a mixture of H_2 and CO) for fuel synthesis. Syngas is typically produced from coal and natural gas and used as a building block in well-known hydrocarbon fuel synthesis processes (e.g. Fischer–Tropsch synthesis). Alternatively CO_2 and H_2O dissociation and fuel synthesis, and even CO_2 capture, might be combined into a single step. Integration of multiple stages can be beneficial e.g. in terms of improved process simplicity and heat management. Some processes aim to combine all of the pieces into a single step (e.g. photochemical or photoelectrochemical dissociation of CO_2 and H_2O that yields hydrocarbons directly from a single unit). However, integration can also result in much more difficult materials requirements, overly tight design constraints, and lower flexibility in operation than using a larger number of steps with each step optimized for its particular function. This will be further discussed in Section 2.2.

Following is a review of work that considers the entire cycle.

The concept of CO_2-recycled synthetic hydrocarbon fuels is not new. Likely spurred by the oil crisis of the 1970s, Steinberg and Dang [3–7] first envisioned the closed-loop version of CO_2-recycled synthetic fuels with CO_2 captured from ambient air. In a series of journal articles and patents, they explored various options to capture CO_2 from the atmosphere using hydroxide or carbonate absorbents, produce H_2 by water electrolysis, and synthesize methanol by reaction of the CO_2 with H_2, with nuclear fission or fusion supplying the electricity and heat. They proposed using the nuclear power plant cooling tower as part of the air capture absorption system. They also considered stripping CO_2 from sea water, and using exhaust CO_2 from industrial plants. Lewis and Martin [8] patented a similar process but with a thermally driven rather than electrically driven CO_2 air capture absorbent regeneration cycle. A similar nuclear powered synthetic fuel process was outlined by Corbett and Salinas [9] followed by its extension to a naval sea vessel with on-board nuclear generator [10]. All of the above processes were based on a low temperature electrolysis dissociation step. Recently, Martin and Kubic [11,12] proposed a slight variation on these processes.

Phillips and Isenberg [13] proposed a different (but also nuclear-driven) process beginning with mineral carbonates (therefore an indirect air capture of CO_2), decomposing them to release CO_2, electrolyzing the CO_2 at high temperature in a solid oxide cell to yield CO, and reacting the CO with steam via a multi-step process to synthesize hydrocarbon fuels. Yamauchi et al. [14] proposed a CO_2-based methanol synthesis process using H_2 from high temperature electrolysis of H_2O, without much consideration as to how the CO_2 would be obtained.

Research on the hydroxide-based air capture processes continued through the 1990s by Bandi et al. [15] and Stucki

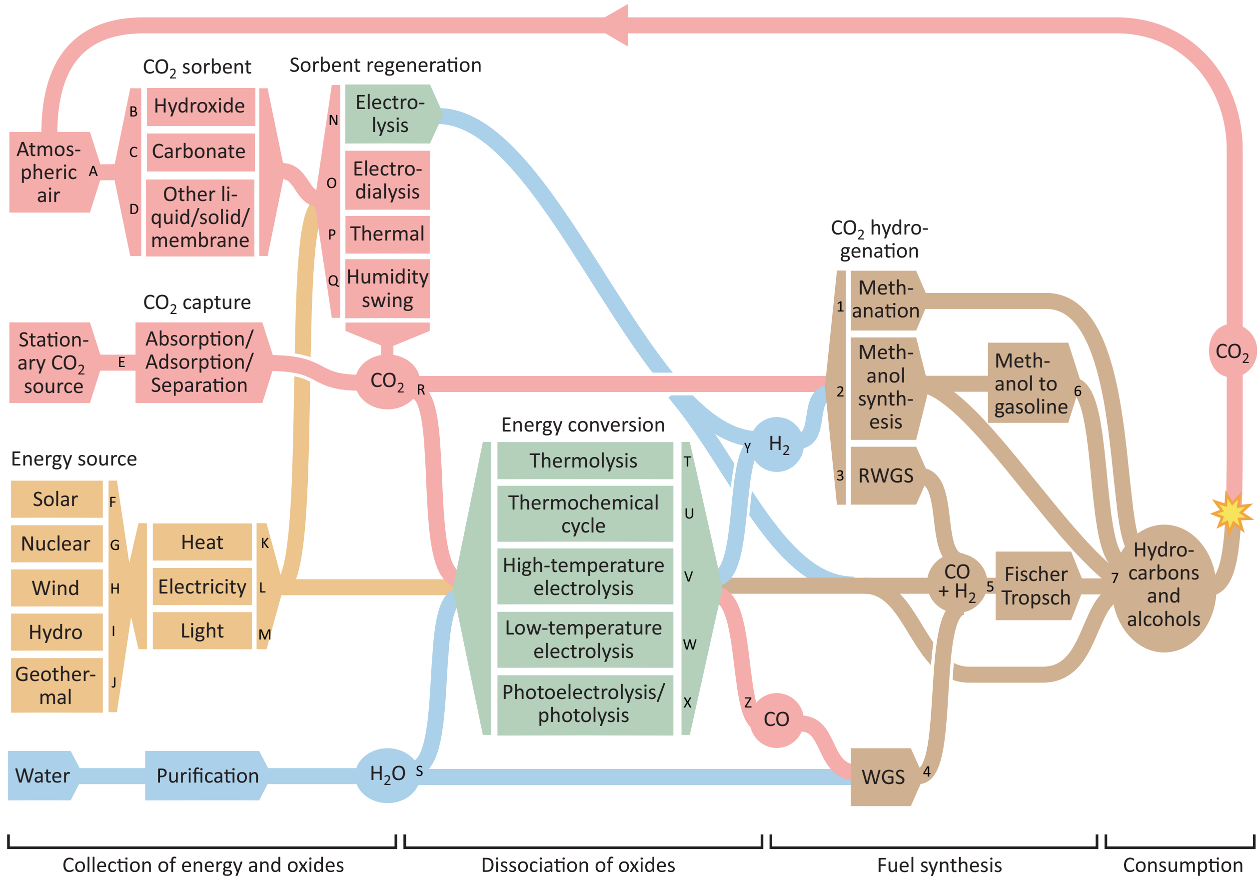


Fig. 3. Map of the possible pathways from H_2O and CO_2 to hydrocarbon fuels. "Fischer–Tropsch" represents any of a variety of catalytic fuel synthesis processes similar to the original Fischer–Tropsch processes.

et al. [16], without the direct tie to nuclear energy or any specific energy source. Weimer et al. (also with Bandi) introduced a solar electricity and heat based process with thermally driven air capture absorbent regeneration and high temperature electrolysis of H_2O [17] or co-electrolysis of H_2O and CO_2 [18] providing the dissociation step.

Hashimoto et al. [19] described a process to produce H_2 by seawater electrolysis powered by solar panels installed in the desert and to synthesize CH_4 by combining the H_2 with exhaust CO_2 collected from industrial plants. Jensen et al. [20–22] have demonstrated a direct solar-driven process that, via combined high-temperature thermolysis and photolysis of CO_2, yields CO for synthetic fuel production. Miller et al. [23] are developing a solar-driven process based on H_2O and/or CO_2 dissociation using ferrites in a thermochemical cycle. They propose to use the resulting H_2 and/or CO for methanol synthesis.

Mignard et al. [24,25] worked out energy balances and cost estimates of several processes for synthesis of methanol and gasoline from industrial waste CO_2 and marine (wind and wave) energy driving the low temperature H_2O electrolysis and fuel synthesis. Olah et al. [26–28] have advocated a "methanol economy" and proposed methanol synthesis by reacting H_2 with air-captured CO_2 or by low-temperature electrolysis of air-captured CO_2 in water to yield syngas followed by methanol synthesis.

Recently there has been a surge of renewed interest in synthetic fuel cycles based on high temperature electrolysis of H_2O, CO_2, or both [29–37]. All of this work has focused on the performance and durability of the electrolysis cells in the dissociation stage of the process. Table 1 summarizes the above review with each full cycle concept mapped to the pathways of Fig. 3, using the letter codes that label each step in Fig. 3. It is evident that the majority of the early work was based on a nuclear energy source ("*G*"), low temperature electrolysis ("*W*"), and methanol synthesis ("2"). More recently the concept has been often based on solar ("*F*") and wind ("*H*") energy and high temperature electrolysis ("*V*").

Zeman and Keith [38] recently reviewed various means of attaining carbon-neutral hydrocarbons, including producing hydrocarbons from a CO_2 feedstock. To produce fuels from CO_2, they advocate using fossil resources. In their proposed CO_2 recycling process, hydrogen is produced from fossil resources in a carbon-neutral manner by capturing and sequestering the CO_2 emissions during the conversion, CO_2 is captured from the atmosphere, and hydrocarbons are synthesized from the H_2 and air-captured CO_2. Although such a process is feasible, it usually does not make sense to use fossil energy in a CO_2 recycling process. The fossil resource already contains carbon in an energetic state. Using this fossil carbon to drive a CO_2 recycling scheme results in generation of more CO_2 which must then be sequestered. The same end result could be achieved by sequestering the captured CO_2 in the first place rather than recycling it. Indeed, their proposed CO_2 recycling pathway is actually an alternate version of the pathway shown in Fig. 2c – producing a fossil-based hydrocarbon and then using off-site air-capture of CO_2 with sequestration to offset emissions from consumption of the fuel – which they also consider. It is more limited and most likely more expensive than the Fig. 2c pathway in that the air-capture site, the fossil resource, and the CO_2 storage site must all be located at the same site or materials must be transported between sites, whereas Fig. 2c pathway enables independent placement of the air-capture device at any appropriate CO_2 storage site. Since the pathway does not actually need CO_2 as a feedstock, it does not fall under the "fuels produced

Table 1
History of work done on the full synthetic fuel cycle concept, using the codes of Fig. 3 to map the pathways. Arrows indicate that the process was integrated into the prior stage. *Italics* indicate that a process was only briefly mentioned.

Years	Reference(s)	Energy collection	CO_2 collection	Dissociation	Fuel synthesis
1970s	[3]	GL	DN	N7	←
	[4]	G(K+L)	(C/D)(N/P)(R+Y)	SWY	27
	[6]	G(K+L)	ER	SWY	267
	[6]	GL	DN(R+Y)	←	267
	[8]	G...	DPR	...Y	(1/2)7
1980s	[9,10]	G(K+L)	DOR	SWY	267
	[13]	G(K+L)	Minerals-PR	RVZ	(Z+S)...7
1990s	[15]	...L	DOR	(R+S)W(Y+Z+1)	27
	[16]	...L	DN(R+Y)	SWY	27
	[14]	G(K+L)	*ER*	SVY	27
	[17,18]	F(K+L)	D(O/P)R	SWY	27
	[18]	F(K+L)	DPR	(R+S)V5	57
	[19]	FL	*ER*	SWY	17
2000s to today	[21,22]	F(K+L)	*ER*	RTZ	457
	[26–28]	...L	DPR	(R+S)W5/SWY	27/57
	[24,25]	(H+I)L	*ER*	SWY	(2/3)(5/6)7
	[33]	...L	BN(R+Y)	(R+S)V5	57
	[11]	G(K+L)	CN(R+Y)	S(W/V)Y	267
	[23]	FK		(R/S)U(Y/Z/5)	57[a]
	[34]	G(K+L)	*Biomass*	(R+S)V5	57
	[35]	(F/H)L	*ER*	(R+S)V5	57
	[29–32,36,37,187]	(F/H/I/J)L	BPR/A...R	(R+S)V5	57

[a] The cited reference does not include fuel synthesis but based on the name of their research program and interviews, the authors have the intention to produce liquid hydrocarbon fuels.

by recycling CO_2" scope. Neither of these carbon-neutral fossil fuel based pathways are materially closed cycles, but they are useful to consider in defining the scope of CO_2-recycled fuels.

In the following sections the work on individual stages of the cycle is reviewed, including greater detail about the individual stages of the full cycle work reviewed above.

2.1. Collection of H_2O and CO_2

Large-scale implementation of any pathway will use large quantities of water. The only sustainable source will be non-potable water such as sea water. To supply the quantity of water needed for dissociation (to provide the hydrogen atoms that get incorporated into the fuel), the cost of desalination will add very little to the synthetic gasoline end product cost – desalinated water is typically produced for less than U.S.D$ 1 m^{-3} [39] which corresponds to only a small fraction of 1 U.S. cent/gal or L of synthetic gasoline. However, water consumption generally can far exceed the water amounts that are needed to provide the hydrogen atoms that get incorporated into the fuel. The required quality of this additional water will depend on the specific processes used. In any case, even if significant quantities of fresh water are needed, it is unlikely that the cost of desalination will make up a significant fraction of the total cost of fuel production. Another proposed source of H_2O is the atmosphere [27]. While perhaps an unnecessary and expensive effort, combined with air-capture of CO_2, both feedstocks would then be extracted from the air, enabling a highly location-independent process.

CO_2 is routinely captured from large industrial plants. The various methods have been reviewed elsewhere [40]. Apart from industrial plants, another non-atmospheric CO_2 source is geothermal vents. Geothermal power plants therefore release this stored CO_2. In Iceland there is interest in managing these CO_2 emissions—including interest in recycling them into fuel [41].

Removing CO_2 from air was first studied in the 1940s by Spector and Dodge using an alkaline absorbent as a means to obtain CO_2-free air [42]. The use of alkaline chemical absorbents has dominated the work done in scrubbing the air to obtain concentrated CO_2. Metal hydroxides such as KOH, $Ca(OH)_2$, and NaOH readily react with CO_2 to form carbonates. Typically hydroxide solutions have been used or proposed [3,6,8–10,15,17,18,32,43–55], and the reaction proceeds as follows:

$$CO_2 + 2OH^- \rightarrow CO_3{}^{2-} + H_2O$$

To release the bound CO_2, the absorbent must then be regenerated with electrical or thermal energy. Alternatively, a carbonate solution has been used to absorb CO_2 [4,5,11,13,56], forming bicarbonate:

$$CO_2 + CO_3{}^{2-} + H_2O \rightarrow 2HCO_3{}^-$$

The CO_2 binds more weakly to a carbonate than to a hydroxide. While absorption into a carbonate requires a longer contact time between the air and the absorbent and/or more of the absorbent, it has the advantage that less energy is needed to release the CO_2 and regenerate the absorbent. In a study comparing the energy demand of several means of air capture, dilute carbonate solution as absorbent was found to require the least amount of energy [4]. However, the absorption rates may be too slow for an economical process.

Other CO_2 absorption media have been examined as well as materials that CO_2 adsorbs onto [4,57]. A variety of geometries for the air contactor have been tested, including packed beds [50] and spray towers [51]. Any process that consumes natural mineral carbonates and leaves behind the oxide or hydroxide form of the mineral could also be considered a method of capturing carbon dioxide from the air, as the waste product is likely to recarbonate with CO_2 extracted from the air. Phillips and Isenberg [13] proposed a process starting from natural mineral carbonates e.g. calcite ($CaCO_3$) to make synthetic fuels with nuclear energy. However, the authors did not consider the possibility of closing the carbon cycle by letting the resulting CaO absorb CO_2 from the air. Nikulshina et al. [58,59] have studied the closed CaO–$CaCO_3$ loop as a thermochemical cycle driven by solar heat, in which CO_2 is captured from the air by carbonating CaO or $Ca(OH)_2$ particles at 350–450 °C (with water vapor introduced to enhance reaction kinetics) and the resulting $CaCO_3$ is calcined at 800–875 °C to release the CO_2.

Once CO_2 has been captured, the absorption or adsorption medium must be regenerated to release the CO_2 and prepare it for capture again. The regeneration of alkaline solutions can be electrically driven via electrodialysis [15,17,43,44] or thermally driven by cycles involving calcination of $CaCO_3$ or other carbonates [8,17,18,45,47,49,50]. Another alternative, electrolysis of the spent absorbent, is an integration of absorbent regeneration and dissociation stages, from which H_2 and O_2 production accompanies release of CO_2 [3,12,16,33]. Since most CO_2-recycled fuel production processes include H_2 production anyway, electrolytic regeneration offers a potentially low energy demand if efficient electrolytic cells are developed. However, the CO_2 and O_2 are disadvantageously released together from the anode compartment of the electrolysis cell, requiring subsequent gas-phase separation. Alternatively a three-compartment cell could facilitate separate release of the CO_2 and O_2 [6,7,33]. An integration of absorbent regeneration and fuel synthesis, by reacting H_2 directly with $CaCO_3$ to yield hydrocarbons, has also been proposed [8].

Recently, a new process involving using a solid adsorbent which is regenerated by a humidity swing has been developed and significantly reduces the energy demands and cost of the process [1]. Whereas thermal air capture cycles have been estimated to need 400–700 kJ heat per mol CO_2 and electrodialysis cycles around 400 kJ electricity per mol CO_2 [50], this process has been estimated to need only 50 kJ electricity per mol CO_2. The cost of air capture has been estimated from as high as \$ 100–200/tonne of CO_2 (tCO_2) [38,49] to a long term cost as low as \$ 30/tCO_2 [1] for this new method.

2.2. Dissociation of H_2O and CO_2

Dissociation of H_2O, CO_2, or mixtures of both is the stage with the largest energy conversion, because this is where the energy is stored as fuel or fuel precursors. The minimum required energy is the enthalpy of the reactions:

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \quad \Delta H_r^{\theta} = 286\,\text{kJ/mol}$$

$$CO_2 \rightarrow CO + \tfrac{1}{2}O_2 \quad \Delta H_r^{\theta} = 283\,\text{kJ/mol}$$

Electrical energy can be used to drive the dissociations via electrolysis. However, heat can generally be obtained at a lower cost than electricity. For example, converting solar energy to heat can theoretically be carried out more efficiently and more inexpensively than photovoltaic (PV) conversion to electricity, which suggests that splitting water in solar furnaces should be preferred over the electrolytic splitting of water. However, using heat for dissociation is a more difficult process, requiring expensive materials that are stable at very high temperature (for thermolysis) or requiring a complicated multiple-step process that needs careful materials handling and heat management at each step (for thermochemical cycles), as will be discussed further in the following sections.

H_2O dissociation for H_2 production has been much more widely researched than CO_2 dissociation. Rather than disassociating the CO_2 directly, hydrogen may be used to reduce CO_2 to CO via the reverse water-gas shift (RWGS) reaction,

$$H_2 + CO_2 \underset{\text{WGS}}{\overset{\text{RWGS}}{\rightleftarrows}} H_2O + CO$$

The same reactants may be used with different conditions and catalysts in hydrogenation reactions to directly produce fuels such as methanol – these have been the most studied reactions in CO_2-recycled synthetic fuel research and will be discussed further in Section 2.3. Alternatively, CO_2 can be dissociated instead, and the resulting CO used to reduce H_2O to H_2 in the water-gas shift (WGS) reaction. Fig. 4 shows the thermodynamics of the dissociation and WGS reactions.

In some cases, splitting CO_2 may have advantages. For example, when the reactant (H_2O or CO_2) should be gaseous, water requires vaporization to steam whereas room temperature CO_2 is already a gas and can be used directly. On the other hand, if low temperature heat (>100 °C) is available to produce steam, the energy consumption of the actual dissociation can be reduced to 249 kJ/mol. Finally, separating the products from unconverted reactants may be easier with H_2/H_2O because the H_2O can simply be condensed to liquid, whereas CO/CO_2 would require gas phase separation.

2.2.1. Thermolysis

It is possible to split H_2O and CO_2 by thermolysis (by the direct use of heat) at extremely high temperatures. The thermodynamics of CO_2 and H_2O dissociation shows that thermolysis occurs fully only at temperatures exceeding 3000 and 4000 °C, respectively (Fig. 4). Literature mentions a temperature range of 2000–2500 °C for H_2O thermolysis [60–62], although the equilibrium constant is only around 0.02 [63] and the product gases, H_2 and O_2, must be separated effectively at high temperature, or rapidly quenched to avoid recombination and then separated at lower temperature. Recombination reduces both the efficiency and fraction of H_2O or CO_2 converted. 2500 °C is a reasonable upper limit because high-temperature ceramics such as zirconia begin to decompose at higher temperatures. Such high temperature heat could be supplied by combustion of fuels in an oxygen or chlorine atmosphere, but for thermolytic fuel production this would be self-defeating since more fuel would be consumed for heat generation than could be produced by thermolysis using the generated heat. Concentrated solar furnaces and a variety of electric furnaces are the two other methods that can provide high temperature heat for CO_2/H_2O thermolysis.

Jensen et al have developed a CO_2 thermolysis chamber driven by concentrated sunlight. CO_2 thermolysis could be carried out at lower temperature than H_2O thermolysis according to the thermodynamics (Fig. 4). In addition, the absorption spectrum of CO_2 is shifted at higher temperatures such that in their chamber the CO_2 is in part photolyzed by the solar irradiation [21]. The observed peak conversion of solar energy to chemical energy was 5%, with expectation of 20% for a mature system [22]. While the demonstrated yield is low, the system also produced unutilized high temperature heat which could be used to drive a steam turbine, giving an additional 25% efficiency for electrical energy [22] (which could be used to produce more CO or H_2 via electrolysis,[3] see Section 2.2.3). If these goals could be met, the total conversion efficiency would be nearly 50%, suggesting a very promising process. However, the majority of energy output from the system is not in the form of thermolysis products but rather electricity, which could have been produced more cheaply. The expensive materials required and complicated gas handling and separations, and heat management, may outweigh the savings from high efficiency. The concentrated sunlight reached ca. 2400 °C in the chamber, indicated by the partially melted zirconia rod at the focal point [22]. The stability of materials can also be strained by thermal shocks due to intermittency of the solar heat source (e.g. rapid transients in sunlight due to clouds). Despite some promising results, because the temperature, materials, and separation requirements for direct solar thermolysis are so severe, development of an economically viable process is unlikely in the near future [61].

An electromagnetic field can be used to excite gaseous H_2O or CO_2 (or at least the electrons in gaseous H_2O or CO_2) to extremely high

[3] Indeed, a study by Baykara [64] concluded that H_2 production by solar H_2O thermolysis is less economical and less efficient than H_2 production by processes in which solar H_2O thermolysis is combined with H_2O electrolysis.

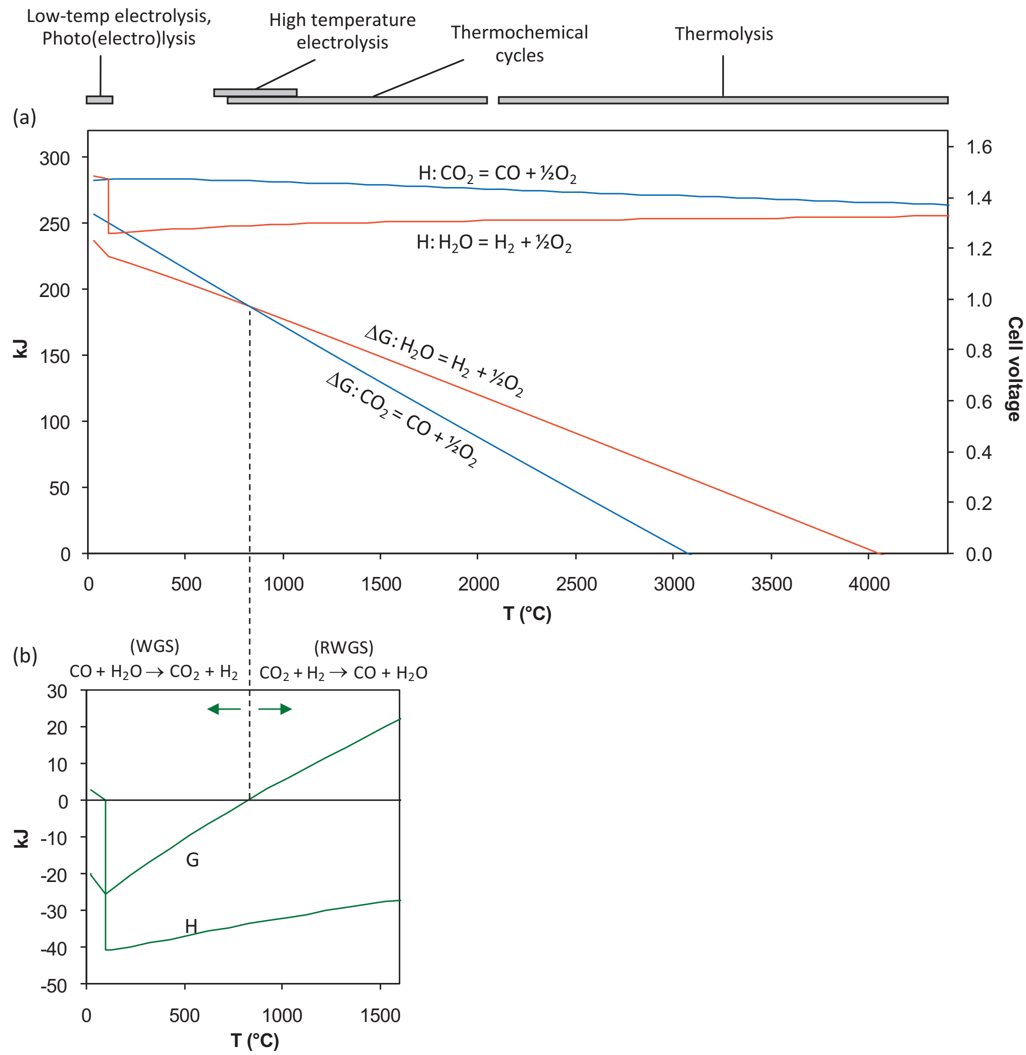


Fig. 4. Thermodynamics of CO_2 and H_2O reduction reactions (a) and water-gas shift (b), using thermodynamic data from [63]. The electrochemical cell potential corresponding to the energy input is on the right vertical axis. The temperature ranges of the various methods of reducing CO_2 and H_2O are also labeled. Note that thermochemical cycles accomplish the reactions indirectly whereas the other methods all directly split the oxide. At temperatures higher than about 827 °C, the free energy of splitting CO_2 is lower than that of H_2O, and correspondingly the reverse water–gas shift (RWGS) reaction becomes favorable.

temperatures (thousands to tens of thousands degrees), which results in plasma based decomposition. In so-called thermal plasmas, the electron temperatures are close to that of the discharge gas, whereas in non-thermal plasmas (also called non-equilibrium or cold plasmas), the electron temperature is far above that of the discharge gas [65]. An advantage of plasma based dissociation over direct solar thermolysis is that the high temperature zone is not in contact with any surfaces, so less expensive materials are needed. However, since plasma based dissociation is driven by electricity, it competes with the other method of electrically driven dissociation, electrolysis. Givotov et al. [66] reported an electricity-to-fuel energy efficiency of 80% for non-thermal plasma decomposition of CO_2, however CO_2 conversion was only 20%, which would require more energy to be spent on subsequent gas phase separation of CO, O_2 and CO_2. Much higher (>90%) CO_2 conversion has been demonstrated using plasma micro-reactors, at the expense of reduced efficiency [67,68]. For plasma decomposition of H_2O, Givotov et al. [66] reported a lower efficiency (<40%) than for CO_2 plasmolysis, with lower conversion as well (<6%). At present, electrolysis is superior to plasma based dissociation because it provides a higher efficiency conversion with the products automatically separated (see Section 2.2.3). However, it is not impossible that plasma-based dissociation could become feasible if the efficiency and rates can be improved and if the cost of the reactors is relatively lower than that of electrolyzers.

2.2.2. Thermochemical cycles

Thermochemical cycles split H_2O or CO_2 through a series of thermally driven chemical reactions at lower temperatures than thermolysis. Product separation is simpler and often inherent in the cycle's reaction steps; one step will yield the H_2 (or CO) and a separate one will yield the O_2. Such cycles can be driven by nuclear reactor heat [69,70] or concentrated sunlight [61,62,71]. Two-step cycles are most often based on reducing a metal oxide while evolving the O_2 in the first step and in the second step oxidizing the metal or lower-valence metal oxide by reaction with H_2O (or CO_2) thereby producing H_2 (or CO):

$$M_xO_y + \text{heat} \rightarrow M_xO_{y-1} + \tfrac{1}{2}O_2(g)$$

$$M_xO_{y-1} + H_2O(g) \rightarrow M_xO_y + H_2(g)$$

The first step requires temperatures up to 2000 °C depending on the cycle. Fewer steps results in lower losses associated with products separation, heat transfer, and transfer of materials between each step. However, there are cycles with three or more steps with a maximum temperature below 1000 °C.

The high temperature (usually 2-step) cycles are considered with concentrated solar heat because concentrated sunlight can provide high temperature heat. The high temperature step places thermal demands on materials, and may require difficult product separation.

Both of these disadvantages are shared with direct thermolysis, because both processes operate at extreme temperatures. The most well-known of this type of cycle is the ZnO/Zn cycle:

$$ZnO(s) \rightarrow Zn(g) + \tfrac{1}{2}O_2(g) \quad 1600-2000\,^{\circ}C$$

$$Zn(s) + H_2O(l) \rightarrow ZnO(s) + H_2(g) \quad 300-400\,^{\circ}C$$

The ΔG_r of the first step is zero at 1982 °C [61]. In the high temperature step, a gaseous phase of the reduced Zn metal is produced. The gaseous Zn and O_2 require quenching to avoid recombination just as in direct water thermolysis. The H_2O (or CO_2) splitting step also has difficulties, including the formation of a passivating layer of ZnO, which reduces the reaction rate [72,73].

Similar two-step cycles aim to overcome these issues, favoring gas–solid separations and/or lower temperatures. The basic ferrite cycle (FeO/Fe_3O_4) enables gas-solid separations, but has proven to be impractical [23,72,74]. Recent investigations have focused on cycles using modified ferrites (substituted with Co, Ni, or Mn) or ceria-based materials as the oxidation–reduction media for dissociation of H_2O to yield H_2 [23,72,75–80], CO_2 to yield CO [23,73,79], or both to yield syngas [79,81–84]. These materials can be reduced at a lower temperature (<1500 °C) and both the oxidized and the reduced phases remain solid, as with the basic ferrite cycle. Ceria and doped ceria are especially interesting materials in that they can release oxygen without a change in crystal structure, cycling between the oxidized oxygen-stoichiometric phase and the reduced oxygen-deficient phase [82]. Ceria-based materials might therefore be expected to retain their microstructure through the redox cycles. Although the microstructure may be redox-stable, the high temperature of the reduction step can lead to coarsening of the microstructure. Grain growth (and a corresponding loss of activity) was observed in porous ceria reduced at 1500 °C – but only during the first 100 cycles, whereafter the performance was stable for hundreds of cycles [79]. Despite the initial performance loss, the high long-term durability suggests that ceria-based materials are a promising thermochemical cycle redox medium. For ferrites and modified ferrites, which are more prone to sintering than ceria-based materials, supporting the material on or combining the material with zirconia or yttria-stabilized zirconia inhibits sintering and improves durability [23,71,74]. Sintering also might not be an issue for some materials. It appears that other ceria-based materials enable a much lower temperature cycle; Cr-doped ceria was recently reported to be significantly reduced at only 465 °C and re-oxidized at 65 °C [85]. Ceria is also a known catalyst for many reactions involving gasses containing carbon and hydrogen [79,85]. Addition of Ni to Sm-doped ceria was found to catalyze direct formation of CH_4 with high selectivity when using a low temperature oxidation step (400 °C) [82]. At other conditions, Ni was found to catalyze the deposition of carbon [82], which might be a desirable product in some cases. Ferrite cycles have also been studied for reduction of CO_2 to carbon [81,86–88]. Finally, it is worth noting that while ceria based materials offer a number of potential advantages, cerium oxides have high molecular weights, which can be a disadvantage since flows of heavy solids should be minimized.

Similar materials have been tested in 3-step cycles with the involvement of hydroxide,

$$M_xO_y + \text{heat} \rightarrow M_xO_{y-1} + \tfrac{1}{2}O_2(g)$$

$$M_xO_{y-1} + 2NaOH \rightarrow Na_2O \cdot M_xO_y + H_2(g)$$

$$Na_2O \cdot M_xO_y + H_2O \rightarrow M_xO_y + 2NaOH(g)$$

e.g. Fe_3O_4/Fe_2O_3 as the reduced and oxidized metal oxides respectively [89]. The introduction of hydroxides is motivated by their higher reactivity compared to that of water which should result in faster reaction rates. The corrosive nature of NaOH, the need to separate liquid $NaOH/Mn_2O_3$ mixtures and the reduced efficiency due to having three steps can each present difficulties.

In all of these high-temperature cycles, thermal management is extremely important to attain an efficient and economical process. With this in mind, research in solar thermochemical cycles also includes the design and development of efficient heat recuperating solar collectors. Rotary reactor systems have been developed to mechanically transport the reactants and to optimize heat exchange between the oxidation and reduction steps [23,75,77,90].

Lower temperature cycles can be suitable for use with heat from nuclear reactors. The 3-step sulfur-iodine (SI) cycle, invented by General Atomics in the 1970s, operates below 1000 °C and has received much attention for integration with heat from high-temperature nuclear reactors [70]. The 4-step calcium–bromine–iron (UT-3) cycle has similarly low operating temperature. The corrosive nature of the chemicals presents material problems. Copper–chloride and magnesium–chloride cycles aim to lessen the corrosion problems of the higher temperature cycles by operating at around 500 °C [69,70]. These cycles have also been proposed as hybrid electrochemical–thermochemical cycles with electrolysis driving one of the reactions in the cycle in order to lower the maximum cycle temperature by enabling a non-spontaneous step [69,70]. While a greater number of steps lowers the maximum temperature needed, each additional step lowers the efficiency as more materials must be handled and more heat must be managed, and multi-step cycles often involve corrosive chemicals.

The above-mentioned cycles are just a few possibilities. Hundreds of possible cycles have been identified for hydrogen production with a variety of maximum operating temperatures [91]. Despite detailed studies of a number of these cycles, they face a number of obstacles: (1) expensive materials (or equivalently, short material lifetimes) associated with high temperatures, rapid temperature transients and/or corrosive chemical intermediates, (2) difficult separations of the chemical intermediates, (3) energy losses across multiple steps from heat exchange, and (4) undesired side reactions. The solar-to-heat conversion efficiency is limited by re-radiation losses and the heat-to-chemicals conversion efficiency is limited by thermodynamics [91,92], with further energy losses from heat recuperation and from separation and quench steps. Practical efficiencies for the net solar-to-chemicals conversion have been estimated in the range of 16–25%, depending on the process [61]. This is in the same range as what can be attained using solar thermal electric or photovoltaic devices coupled to electrolyzers. The economic benefits from the slightly higher efficiency of a thermochemical process may easily be outweighed by the economic cost of exotic materials. An economic estimate based on hydrogen production using the latest promising thermochemical cycles versus using commercial alkaline electrolysis cells concluded that, when driven by the same concentrated solar thermal power source, the technologies have comparable costs [93]. The achievable electrolysis cost for a given electricity cost may be lower than estimated in that study because high temperature electrolysis has the potential to be significantly cheaper than today's commercial alkaline electrolysis [31].

2.2.3. *Electrolysis*

An electrolysis cell dissociates H_2O or CO_2 using electricity. Attractive in its simplicity, electrolysis performs the dissociation in a single step without any need for moving parts, and the products are released separately in the anode and cathode compartments of the cell. For solar conversion, a PV cell could be coupled to an electrolysis cell, which would comprise a full system without moving parts. Thermolytic and thermochemical reactors, on the other hand, need a mechanical sun-tracking system to concentrate the direct incident sunlight to collect high temperature heat. Electrolysis cells, like photovoltaic cells, are ideal for mass production and automated maintenance.

An especially interesting property of an electrolysis cell is the ability to choose the efficiency at which it operates. For example, the enthalpy of H_2O dissociation corresponds to a cell voltage of 1.48 V whereas the free energy corresponds to a H_2O electrolysis reversible potential of 1.23 V at 25 °C and 0.96 V at 850 °C (Fig. 4). Assume for a moment that the internal resistance is a constant 1 Ω at any applied voltage for both a low-temperature cell (25 °C) and a high-temperature (850 °C) cell, and that the open-circuit voltages (OCV) are at the reversible potentials.[4] Then, isothermal operation of the cells, by applying the thermoneutral voltage of 1.48 V,[5] yields currents of 0.25 A [=(1.48 − 1.23 V)/1 Ω] and 0.52 A [=(1.48 − 0.96 V)/1 Ω], respectively. Both cells are being run at 100% efficiency in electricity-to-chemical energy conversion. From the higher rate of hydrogen production it is clear the high temperature cell has an advantage – even for the same internal resistance, more hydrogen is being produced because part of the dissociation energy is supplied as heat (the difference in ΔH and ΔG shown in Fig. 4), which is being supplied as the inevitable Joule heat produced by the internal electrical resistance of the cell (alternatively, high-temperature heat from an external source could be used to supply part of the heat demand). The advantage is further boosted because in reality high-temperature cells nearly always have lower internal resistance than low-temperature cells—even with equivalent catalytic activity, higher reaction rates are achieved because the reactions are thermally activated to a greater degree. These differences between low and high temperature electrolysis cells can be seen in the polarization curves illustrated in Fig. 5.

The cost of hydrogen produced by H_2O electrolysis, C_{H_2} (in $/GJ), can be estimated as follows:

$$C_{H_2} = C_{op} + C_{cap}$$

$$C_{op} = \frac{C_{electricity}}{\eta_{electrolysis}} + C_{O\&M} \qquad C_{cap} = \frac{C_{investment}}{Q_{H_2\,prod}}$$

$$\eta_{electrolysis} = \frac{E_{th}}{E_{op}} \cdot \eta_{current} \qquad C_{investment} = \frac{C_{stack}}{t_{stack\,life}} + \frac{C_{bal\,of\,sys}}{t_{sys\,life}}$$

$$E_{th} = \frac{\Delta H_{f,H_2O(l)}}{n \cdot F} \qquad Q_{H_2\,prod} = I \cdot f_{util} \cdot \frac{\Delta H_{f,H_2O(l)}}{n \cdot F}$$

$$I = i \cdot A_{cell} = \frac{E_{op} - E_{Nernst}}{ASR} \cdot A_{cell}$$

where C_{op} is the operating cost and C_{cap} is the capital cost of the entire electrolysis system. These costs are in turn given by the above expressions in which $C_{electricity}$ is the cost of electricity, $\eta_{electrolysis}$ is the electricity-to-chemical energy conversion efficiency at which the electrolyzer is operating,[6] $C_{O\&M}$ is the operating and maintenance cost per unit of output, E_{th} is the thermoneutral voltage of water electrolysis, E_{op} is the cell operating voltage, $\eta_{current}$ is the current efficiency (the fraction of the current that drives the desired reactions) which is very close to 100% for all types of state-of-the-art electrolysis cells, $\Delta H_{f,H_2O(l)}$ is the enthalpy of formation of water (or equivalently, the enthalpy of the water electrolysis reaction, or equivalently the higher heating value (HHV) of hydrogen), n is 2 (mol of electrons per mol product H_2 in the electrochemical reaction), F is Faraday's number (96485 C/mol), $C_{investment}$ is the investment cost of the system including financing, Q_{H_2prod} is the average rate at which H_2 is produced in kW, C_{stack} and $t_{stack\,life}$ are the investment cost and lifetime of a cell stack respectively, $C_{bal\,of\,sys}$ and $t_{sys\,life}$ are the investment cost and lifetime of the balance of system respectively, I is the cell operating current averaged across the cell's operating life, f_{util} is the fraction of time the cell is utilized over its life (sometimes called the capacity factor), i is the current density (e.g. A/cm^2), A_{cell} is the active area of the cell, E_{Nernst} is the equilibrium Nernst potential at the given conditions, and ASR is the internal area-specific resistance of the cell averaged across the operating life.

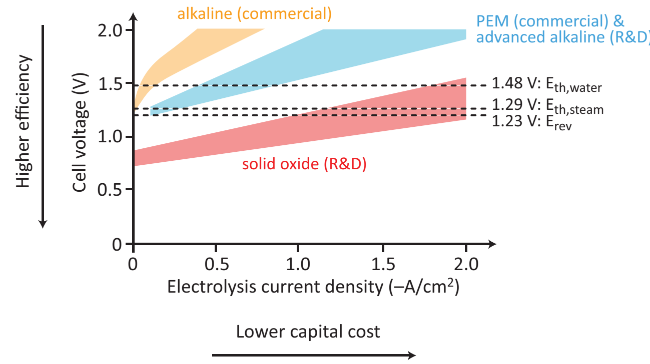


Fig. 5. Typical ranges of polarization curves for different types of state-of-the-art water electrolysis cells. $E_{th,water}$ and $E_{th,steam}$ are the thermoneutral voltages for water and steam electrolysis, respectively. E_{rev} is the reversible potential for water electrolysis at standard state. These curves are representative based on [31,35–37,94–99,107–109,160,187,232,240,241].

This is a simplified method which assumes time-averaged parameters; in reality, many of the parameters vary with time. Clearly, $C_{electricity}$ varies with time regardless of the source. $\eta_{electrolysis}$ might vary with time depending on how the electrolyzer is being operated; if potentiostatic operation (constant E_{op}) is used throughout the operating life then the efficiency will not vary with time. $C_{O\&M}$ varies with time e.g. as unexpected events occur such as equipment failures. $C_{investment}$ may vary with time as the interest rate may vary during amortization. The time variability of the cell operating current I may be one of the most important parameters in terms of its potential impact on the capital cost. In reality I, t_{life} and f_{util} are encompassed together in the equation $\int_0^{t_{life}} I(t)dt$. Intermittency $(1 - f_{util})$ of the power supply results in start-stop operation and/or smoother time-varying current operation. Cell degradation also affects $I(t)$. For example, for constant-voltage operation the current will decrease over time as the internal resistance increases due to cell degradation. Degradation may also be compensated for to maintain current density, e.g. by increasing the cell voltage (slightly lowering the efficiency) or the operating temperature. Depending on the intermittency, the degradation rate, the electricity price, and the investment cost, the $I - E_{op}$ operating point may be varied during the cell lifetime to optimize for the lowest H_2 production cost. Finally, t_{life} may also depend on the functional form of $I(t)$. For example, the end of life may be declared when the operating current drops below half of the initial operating current due to degradation.

The operating current I or $I(t)$ and corresponding cell voltage must be included in any economics estimation that involves variability with time, e.g. intermittency of a renewable or surplus power supply or a time-varying electricity price. Estimates in the literature that present the capital cost in terms of per watt of

[4] This assumes that the activities or partial pressures of the reactants and products (H_2, O_2, and H_2O) are such that the Nernst potential is the same as the reversible potential—that the equilibrium constant in the Nernst equation is 1, e.g. for a high temperature cell, $pH_2/pH_2O = 1$ and $pO_2 = 1$ are assumed. In reality, for practical implementation it would be desirable to supply a much higher H_2O content, e.g. pH_2/pH_2O should approach zero, resulting in an OCV lower than 0.96 V, which would increase the current to greater than 0.52 A in the calculation that follows.

[5] Note that the high temperature cell is electrolyzing steam. The thermoneutral voltage for the steam electrolysis reaction at 850 °C is 1.29 V, but the thermoneutral voltage for the cell is still 1.48 V if one includes the heat exchanger that is needed to generate steam for the cell if liquid water is the input.

[6] Since the electrolysis efficiency is defined as the thermoneutral voltage over the operating voltage and the cell can be operated at a lower voltage than the thermoneutral voltage (where the cell internal resistance does not supply enough heat), theoretically efficiencies greater than 100% are possible if external heat is available to supply the remaining energy required. However, such an external heat supply must be accounted for in the system energy balance, therefore the system will have an upper limit of 100% efficiency. The heat could be supplied by external electrical heating, giving 100% as the upper limit for the net efficiency of electricity to chemicals for the system.

hydrogen produced are already optimized for a certain type of operation – usually near-constant operation (at near-100% capacity factor), e.g. including cell degradation but insignificant intermittency.

The cost is optimized between the capital cost and the operating cost. Although it is possible to operate any electrolyzer at near-100% electricity-to-chemical energy efficiency, it is not always economically optimal to do so; some cells cannot attain a sufficiently high current density at the thermoneutral voltage. In that case, it would be desirable to operate a cell at lower than 100% efficiency ($E_{op} > E_{th}$, resulting in excess heat being generated in the cell) if the larger operating voltage (E_{op}) is needed in order to achieve a higher hydrogen production rate (higher current density). For example, commercial alkaline electrolyzers are typically operated at 1.8–2 V (around 70–80% efficiency based on the higher heating value of H_2) at 0.2–0.5 A/cm^2 [94–99]; they are run at non-optimal efficiency. This operating point is chosen due to the low current density attained at lower operating voltages, evident in the polarization curve (Fig. 5). Some efficiency is sacrificed to lower the capital cost. This can explain why it is often cited that electrolysis can be performed with "up to 73% efficiency" [97] – based on the materials and system cost, lifetime, capacity factor, and internal resistance of the alkaline cells being referred to, the lowest cost operation is at an operating voltage of about 2 V (=1.48 V/73%). This current–voltage (i–V) operating point is optimal for the investment cost of the cells, the known degradation rate of the cells, a near-100% capacity factor and a specific electricity price. Intermittent operation (e.g. running on intermittent solar or wind power) increases the capital cost of the electrolyzer and therefore results in a lower efficiency optimum i-V operating point.

In the design, manufacture and operation of an electrolysis system, four parameters can be controlled:

Affecting the operating cost, C_{op}:

1. the energy efficiency (via the operating voltage, E_{op}),

Affecting the capital cost, C_{cap}:

2. the cost of producing the cell stack and balance of system, $C_{investment,}$
3. the operating current density, i,
4. the operating lifetimes $t_{stack\ life}$ and $t_{sys\ life}$.

For the most economical hydrogen production, E_{op} and $C_{investment}$ should be as low as possible and i and t_{life} should all be as high as possible (and since E_{op} and i are proportional and inversely proportional to the ASR, respectively, the ASR should be as low as possible). In other words, the cells should be cheap to produce and run efficiently at high throughputs for a long time.

2.2.3.1. Low-temperature electrolysis. Alkaline water electrolysis cells are the dominant type of cells in commercial operation today [97,100,101]. The electrode reactions are:

$$\text{Cathode}: \quad 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

$$\text{Anode}: 2OH^-(aq) \rightarrow 2e^- + \tfrac{1}{2}O_2(g) + H_2O(l)$$

The electrolyte is typically a 30 wt% KOH solution and the operating temperature is 70–100 °C. The electrodes are typically porous Raney nickel electrodes which are formed by electrodeposition of a Ni–Al or Ni–Zn alloy onto a metallic (often mesh) substrate followed by leaching of the Al or Zn by a strong hydroxide solution, leaving behind a porous Ni structure. Alkaline electrolysis cells are operated with an efficiency and current density as described just above. Alkaline cells, operated in the reverse direction as fuel cells, were developed and used for space exploration since the 1960s [102]. Alkaline cells have a potential economic advantage in the ability to easily replace each cell rather than the entire stack as in other cell types. The durability of alkaline electrolyzers is sufficiently high, giving a typical operating life of 10–20 years [97,100,101]. For the latest commercial cells, durability was not found to suffer greatly when operating on intermittent renewable electricity (older technology suffered degradation while resting at open circuit conditions for extended periods of time). However, the capital cost for an alkaline electrolyzer stack and system has been estimated at $ 7.5–9/GJ of H_2 produced, assuming near-100% capacity factor operation [97,100,103]. Intermittent operation increases the capital cost significantly even with optimization of operation (sacrificing efficiency to increase the current density). Alkaline electrolyzers may become viable if the manufacturing cost can be reduced to a small fraction of what it is now.

Advanced alkaline electrolysis cells are at a pre-commercial stage. Such cells are typically operated at higher temperature and/or higher pressure [94,95,100,104–110] which both enhances the current density at a given cell voltage and yields high-pressure hydrogen, which is needed in any case for the subsequent fuel synthesis reactors. Advanced cells also often have micro- or nano-structured electrodes made up of higher surface area nickel, alloys or composites containing nickel, or ceramic materials to improve current density [19,109,111–113]. Long-term durability of advanced alkaline electrolysis has been demonstrated [109,114].

Since seawater is naturally alkaline, seawater electrolysis can use modified alkaline electrolysis cells [19]. The cells must be modified to avoid evolution of chlorine gas. Although seawater electrolysis is in fact conventionally used to produce chlorine, the scale of electrolysis operation needed to produce the fuels needed to satisfy the world's demand for transportation fuels would exceed world demand for chlorine by many orders of magnitude. Therefore, due to the toxicity of chlorine, oxygen would be the preferred anode product from a seawater electrolysis cell. Since the anode potential for oxygen evolution is lower than that of chlorine evolution, the cell must be operated with an anode potential within a range above the oxygen evolution potential and below the chlorine potential. Therefore, new anode materials such as Mo- and W-doped MnO_2 are being developed to achieve high anodic efficiency [111]. However, it may be unnecessary to deal with seawater in an electrolysis cell since obtaining pure water by desalination adds only a negligible cost to the fuel production process, as discussed in Section 2.1.

Related to alkaline electrolysis is the co-electrolysis of H_2O and CO_2 using aqueous carbonate or bicarbonate electrolyte [15,115–123]. The CO_2 can be supplied by being bubbled in or dissolved in the aqueous media, or supplied from the gas phase to a gas diffusion electrode. The majority of research in aqueous co-electrolysis of CO_2 and H_2O has focused on improving current efficiency (product selectivity) at a given potential rather than maximizing energy efficiency (for lower operating cost) or current density (for lower capital cost). The CO_2 and H_2O are electrocatalytically reduced to products such as HCOOH, CO, CH_4, C_2H_4, and higher hydrocarbons and alcohols, depending on the cathode composition and cell parameters. For example, copper electrodes were found to selectively produce methane, methanol and other hydrocarbons over just H_2 and CO, whereas Au and Ag selectively produce CO [115,116,119]. The cathode reaction for methanol is as follows:

$$CO_2(aq) + 6H^+ + 6e^- \rightarrow CH_3OH(l) + H_2O(l)$$

Cu and Ag metal electrodes have shown low durability due to accumulation of carbon particles during CO_2 reduction [124–126]. Metal alloy cathodes were shown to have increased durability and inhibit poisoning over pure metals [127,128]. Reactivation of the electrodes by briefly pulsing an anodic current has also been explored [128–131]. Electrodes made of transition metal com-

plexes [120,132], e.g. phthalocyanine–Co/Ni, are able to coordinate the CO_2 molecule and electrocatalytically reduce it with high selectivity (but not high efficiency). Though they have lower durability, their promise lies in being less expensive than pure metals. Because the solubility of carbon dioxide in water (~0.036 M at STP) is low, rate limitation from mass transport of CO_2 to the surface results in limiting current densities of -10 to -20 mA/cm^2 under 1 atm CO_2 [133,134]. Electrolyzing bicarbonate, which has a higher solubility (~1 M) than CO_2, has not been found to enhance the reaction rate. Gas diffusion electrodes enable higher current densities. Centi et al. [122,123] reported the production of CO and small fractions of various long-chain C_{5+} hydrocarbons at a gas diffusion electrode. However, they used an electrode with expensive Pt and Pd nanoclusters, and found the maximum product selectivity was at the low current density of -20 mA/cm^2.

Overall, the overpotentials needed (to either selectively produce such hydrocarbon products or to produce H_2/CO) are at present too high for a viable electrolyzer. With these types of cells, reasonable current densities have only been achieved at a very low efficiency – a current density of -100 mA/cm^2 requires application of about 3 V to produce a mixture of methane and hydrogen with small amounts of ethylene and carbon monoxide [121] or a mixture of potassium formate and hydrogen [135]. This results in an impractically high operating cost in comparison with other types of cells (Fig. 5). Therefore, a cell with such a high internal resistance would need to be run at higher efficiency (lower current density). The current density at a given efficiency is a factor of 100 lower than higher performance cells, so the capital cost must be a factor of 100 lower to be competitive. As such an extremely low capital cost (via very cheap materials and/or very long lifetime) seems unlikely, this technology needs a significant breakthrough in reaction rates to be feasible. Perhaps state-of-the-art alkaline water electrolysis cells (or advanced alkaline cells operating at elevated temperature and pressure) could be modified to work more effectively for aqueous co-electrolysis (or H_2O electrolysis combined with catalytic CO_2 hydrogenation to hydrocarbons at a gas diffusion cathode).

Proton exchange membrane (PEM) cells operate at a similar temperature range and are also commercially available. In PEM cells, protons are selectively conducted across a polymer membrane and the following electrode reactions take place:

$$\text{Cathode}: \quad 2H^+(aq) + 2e^- \rightarrow H_2(g)$$

$$\text{Anode}: H_2O(l) \rightarrow 2H^+(aq) + 2e^- + \tfrac{1}{2}O_2(g)$$

Because PEM cell electrodes contain expensive noble metal electrocatalysts (typically Pt particles) and expensive membranes their capital cost is higher than that of alkaline cells. To compensate for this higher cost, they are operated at higher current density (Fig. 5). With IrO_2 and Pt electrodes, Yamaguchi et al demonstrated -1 A/cm^2 current density at 1.54 V at 80 °C under atmospheric pressure [136]. Such high current densities do not seem to be high enough to offset the cost of the expensive materials; at present, high capital cost appears to be an obstacle to affordable PEM-based electrolysis. Less expensive materials are needed.

Recently an interesting method of preparing an inexpensive water electrolysis oxygen-evolving anode was reported by Nocera and co-workers [137,138] wherein a catalyst layer bearing Co or Ni is formed in situ on an inert surface from a near-neutral pH aqueous solution. A very thin layer – perhaps even a monolayer – of the catalyst might suffice and the benign electrolyte does not demand expensive materials for the cell components and housing. Therefore, if a similar hydrogen-evolving cathode can be developed, this type of cell might be cheap to produce. However, these electrodes produce H_2 at only 1 mA/cm^2 at an overpotential of >400 mV. As this current density is more than 100 and 1000 times lower than that of alkaline electrolysis cells and high temperature electrolysis cells respectively, the cost per unit electrode area of this type of electrolysis system would have to be more than 100–1000 times lower than the other electrolysis systems to be competitive in terms of H_2 production price, assuming they have a similar operating life. However, the operating life of this type of cell might be significantly longer due to the possibly self-healing nature of the catalyst layer which is constantly re-forming on the surface. Furthermore, due to the potentially simple construction and materials requirements of the cell, the cell production cost could indeed be orders of magnitude lower than the other cell types, and future electrode designs might yield improved current density. This electrode technology and cell type is at a very early stage of research. Further study and development of this type of cell is necessary to assess economic viability.

Electrolyzing CO_2 in non-aqueous organic solvents such as methanol or acetonitrile can yield CO [117,132] via the cathode reaction

$$2CO_2 + 2e^- \rightarrow CO + CO_3{}^{2-}.$$

Similarly, electrolysis of supercritical CO_2 has also been examined. Pure supercritical CO_2 exhibits zero or negligible conductivity, so electrolytes composed of additives dissolved in supercritical CO_2 [15] or ionic liquids (as solvent and electrolyte into which supercritical CO_2 is dissolved) [139] have been studied. Co-production of CO and H_2 via electrolysis of supercritical CO_2 and water dissolved in an ionic liquid electrolyte has been initially demonstrated [139]. The large overpotentials observed in that study may be the result of the use of a basic unoptimized cell, so at present it is difficult to assess the potential of this method.

2.2.3.2. High-temperature electrolysis. As mentioned earlier, performing electrolysis at high temperature has both a thermodynamic advantage and an advantage in reaction rates. With increasing temperature, a larger portion of heat and corresponding smaller portion of electricity is needed for the dissociation. This can be seen in the lower open-circuit voltage for the high temperature cells in Fig. 5. This heat can be supplied from external sources, or it can be the Joule heat that is inevitably produced, due to the internal electric resistance of the cell, when applying the overvoltage necessary to achieve sufficient production rates. Rather than losing this ohmic heat, it is used in the disassociation of steam and/or CO_2. High temperature electrolysis therefore relies in part on thermolysis pushing the equilibrium toward dissociation. The high temperature also results in faster reaction kinetics which reduces the need for expensive catalyst materials. These differences between low and high temperature electrolysis cells can be seen in the polarization curves illustrated in Fig. 5. These advantages enable very efficient operation (at near the thermoneutral voltage) at very high current densities (potentially leading to low capital cost).

There are two types of high temperature electrolyzers (typically >600 °C operation), those with molten carbonate electrolytes and those with solid oxide electrolytes. Since the electrolytes of solid oxide electrolysis cells (SOECs) and molten carbonate cells conduct O^{2-} and $CO_3{}^{2-}$ ions respectively, they can electrolyze CO_2 to CO in addition to H_2O to H_2. However, electrolysis using molten carbonate cells to produce H_2 or CO carries a disadvantage, in that a mol of CO_2 is effectively transported across the cell for every mol of fuel produced:

$$\text{Cathode}: \quad H_2O(g) + CO_2(g) + 2e^- \rightarrow H_2(g) + CO_3{}^{2-}$$

$$\text{or} \quad 2CO_2(g) + 2e^- \rightarrow CO(g) + CO_3{}^{2-}$$

$$\text{Anode}: \; CO_3{}^{2-} \rightarrow 2e^- + \tfrac{1}{2}O_2(g) + CO_2(g)$$

This CO_2 is released at the anode along with O_2, resulting in a mixed product stream there. Additional energy must then be spent to separate the CO_2 and O_2, as the CO_2 can of course not be released to the atmosphere, and the CO_2 will be needed again for the cathode reaction. The only report of such molten carbonate based electrolysis was a preliminary report made by a NASA research group with the intention to electrolyze CO_2 from the CO_2-rich atmosphere of Mars to produce breathable oxygen [140].

Recently, direct electrolysis of molten carbonate to produce CO and O_2 was reported [141]. The cell used differs from that of the above-mentioned molten carbonate cells in that molten carbonate is not only the electrolyte but the reactant as well:

$$\text{Cathode}: \quad CO_3{}^{2-} + 2e^- \rightarrow CO(g) + 2O^{2-}$$

$$\text{Anode}: \; CO_3{}^{2-} \rightarrow 2e^- + \tfrac{1}{2}O_2(g) + CO_2(g)$$

The oxide ions that are produced at the cathode facilitate re-absorption of the CO_2 produced at the anode as well as re-absorption of additional CO_2:

$$2CO_2(g) + 2O^{2-} \rightarrow 2CO_3{}^{2-}$$

Indeed, the amount of CO_2 measured at the anode outlet gas stream was less than 0.005 atm. This cell type therefore does not have the problem of separating CO_2 from the output oxygen stream. The authors state that CO_2 at a partial pressure of just a few percent can be absorbed from the feed gas stream by the carbonate melt. The current densities attained are low (<100 mA/cm^2) and the long-term durability is unknown, but the electrode and container materials are inexpensive (only titanium and graphite) and the performance of the cell has not been optimized. Both types of molten carbonate cell technology share the disadvantage that the molten carbonate is corrosive which limits the choice of stable materials for the electrodes and other components.

Solid oxide electrolysis cells (SOECs) do not suffer from the above problem. Their electrode reactions are (depending on whether they are operating on steam or CO_2 input feed streams):

$$\text{Cathode}: \quad H_2O(g) + 2e^- \rightarrow H_2(g) + O^{2-}$$

$$\text{or} \quad CO_2(g) + 2e^- \rightarrow CO(g) + O^{2-}$$

$$\text{Anode}: \quad O^{2-} \rightarrow 2e^- + \tfrac{1}{2}O_2(g)$$

As with low-temperature electrolysis, cells designed as solid oxide fuel cells (SOFCs) can be used reversibly for electrolysis. However, due to differing conditions (the gas compositions at the electrodes and the direction of polarization across cell components and across interfaces between materials) between fuel cell and electrolysis operation, it may be desirable to make specialized cells for optimal electrolysis performance.

Electrolysis of CO_2, H_2O, and co-electrolysis of CO_2/H_2O mixtures using solid oxide cells was first demonstrated in the 1960s under NASA contracts, for the purpose of O_2 production for life support and propulsion in submarines and spacecraft [142–147] and research on using the cells for this purpose continues to this day [148–153]. The first solid oxide electrolysis research project unrelated to space exploration appears to be the HOT ELLY project in Germany started in 1975 [154], which focused on H_2 production. The most common material composition of typical state-of-the-art SOECs today were already being used – a porous metal-ceramic Ni-YSZ composite cathode and a porous ceramic composite anode composed of lanthanum strontium manganite and YSZ, sandwiching a dense ceramic YSZ electrolyte (YSZ = yttria-stabilized zirconia, a material that conducts O^{2-} ions at high temperatures). The performance, durability and materials used in high temperature electrolysis cells have been recently reviewed [107,155]. A variety of alternative materials with improved properties for SOFCs are under development [156–159], many of which might be appropriate for use in SOECs. Much work has been done in testing cells and optimizing electrode and electrolyte materials for steam electrolysis [31,160–183], CO_2 electrolysis [13,31,32,148,160,175,182,184–188], and co-electrolysis of both H_2O and CO_2 simultaneously to produce syngas [18,29,33–37,175,182,189–191]. In co-electrolysis, CO_2 may be either electrolyzed or indirectly split via reverse-WGS. One can see in Fig. 4 that the WGS equilibrium can go either way at the operating temperatures of an SOEC. Since CO_2 electrolysis has a slightly higher resistance than H_2O electrolysis [31,34–37,160,175,187], it is expected that part of the CO produced results from RWGS. Whether part of the syngas is produced by the WGS equilibrium has little effect on the energy demand of syngas production in the cell, because the cell's internal resistance can supply the heat needed for either the electrochemical or catalytic reactions. Systems integrating steam SOECs with solar [17,18,192–194] and nuclear energy [70,195] have been examined and SOECs have been proposed for use in CO_2-recycled synthetic fuel cycles [14,17,18,33,36,37,182,188].

A high current density of -3.6 A/cm^2 was reported when operating an SOEC for steam electrolysis at 950 °C at 1.48 V [31]. At 850 °C a similar cell showed area specific resistances (ASRs) of 0.19 and 0.24 Ω cm^2 for H_2O electrolysis and CO_2 electrolysis respectively, measured from open circuit to -0.16 A/cm^2 [36]. In recent studies of co-electrolysis of H_2O and CO_2, the ASR was in between that of H_2O and CO_2 electrolysis [34–37].

The long-term durability of SOECs has been a topic of recent studies [36,37,169,175–180,182,183,187,188]. At least at lower current densities, the cells were found to have sufficient durability for co-electrolysis of H_2O and CO_2 [36,37]. In fact, exceptional durability was recently reported – for current densities up to -0.75 A/cm^2, operation with little or no degradation at all was attained by removing impurities from the inlet gasses [182,188]. At higher current densities, however, the cells still degrade [37,183]. Durable high current density operation will be desirable and perhaps necessary for an economical process, based on the economics discussion above (see also Section 3.2). Therefore, further work in improving the durability may be necessary. The instability of the Ni-based electrode when exposed to an oxidizing atmosphere is also an issue that may need resolution before large-scale commercial use of these cells. With current cells, it would be necessary to ensure that the Ni-based electrode of each cell is always kept in a reducing atmosphere through all gas supply interruptions and unexpected incidents during operation, e.g., the cell would require a fail-safe gas recirculation system. However, depending on the cell construction [196–198] and the temperature at which an oxidation event occurs [199,200], the performance of cells with Ni-based negative electrodes may be largely unaffected through tens of such events. Alternatively, electrodes based on ceramic materials that exhibit higher stability through reduction-oxidation (redox) cycles and similarly high electrocatalytic activity as Ni-based electrodes have been developed and demonstrated in small-scale cells [145,187–189]. If this type of redox-stable electrode can be integrated into a full-scale commercial cell, replacement of the Ni-YSZ electrode with this type of alternative electrode would likely be the preferred solution to this issue.

While higher temperature operation enables greater fuel production rates, it can result in performance degradation by damaging the electrode structures via sintering and agglomeration as well as putting strain on the cell interconnect, housing and other materials that make up the balance of system components. Lower temperature operation disadvantageously increases the thermodynamic electrical energy demand and requires more electrical energy per unit fuel produced (slower kinetics), but also enables the survival of optimized microstructures and nanoparticles

(which promote faster kinetics) against sintering and agglomeration, thereby potentially evening out the cell performance. Lower temperature also retards Ni oxidation, potentially improving the stability of the Ni electrode, as mentioned above. Therefore, there is likely an optimal operating temperature for a given cell based on its materials, construction and performance.

The estimated investment cost of a solid oxide cell stack per unit of electrode area is about the same as that estimated for low-temperature alkaline and advanced alkaline electrolyzer stacks at large-scale mass production [94,100,201–203], and the H_2/CO production rate is much higher, leading to a lower capital cost. Solid oxide cells clearly offer both the lowest capital cost and the lowest operating cost. Furthermore, since solid oxide electrolysis cells can produce syngas directly via co-electrolysis of H_2O and CO_2, they reduce the system cost by eliminating the need for a RWGS reactor in the CO_2-recycled fuel production process. They also enable an improvement in the net system efficiency via utilization of the waste heat of exothermic Fischer–Tropsch type reactors that would be used for fuel synthesis (this is further examined in Section 3.1). However, heat management is more complicated for these high temperature cells and can more easily lead to energy losses, as well as higher capital costs due to materials and equipment failures or simply additional system costs that have been underestimated. Finally, durable performance at the high current densities that may be necessary remains yet to be proven.

2.2.4. Photoelectrolysis

While an electrolysis cell could be powered by a PV source, an interesting combination of the two is a photoelectrochemical (PEC) cell for hydrogen production [99,204]. Such a cell has as either its anode or cathode a semiconductor photoelectrode immersed in an aqueous solution. The photoelectrode collects photons creating excited electrons which electrolyze water molecules at the interface with the aqueous electrolyte. At the interface, the electrode can be coated with an electrocatalyst that enhances the electrolysis reaction.

In principle, such integration reduces the system capital cost and enables higher efficiency by reducing the losses in transporting electricity from the PV cell to the electrolysis cell, eliminating current collectors and interconnections between devices. In practice, several characteristics of the photoelectrode must be satisfied simultaneously: the electronic band gap of the photoelectrode must be low enough for efficient photon collecting from the solar spectrum (<2.2 eV) and high enough such that the excited electrons have enough energy to split water (>1.23 eV or typically at least 1.6–1.7 eV for sufficient rates), the band edges must straddle the water electrolysis redox potentials, and the photoelectrode must be stable and resistant to corrosion in the aqueous electrolyte [204]. These constraints rule out most inexpensive, conventional PV, yet the photoelectrode should also have a similar photoconversion efficiency as conventional PV to give this option an advantage over a PV-electrolysis system made up of separate units. Research focuses on a multitude of electrodes, including semiconductor oxides such as TiO_2, $CaTiO_3$, $SrTiO_3$ and composite oxides tailored to yield appropriate band gaps, and multijunction cells with two or more semiconductor layers, e.g. Si as one layer with the other layer (GaInPN, $CuGaSe_2$, etc) protecting it from corrosion.

Sunlight-driven dissociation of H_2O directly on TiO_2 is an active field of research. However, the broad band gap of TiO_2 limits the efficiency of absorbing sunlight [205]. Several approaches to widen the wavelength sensitivity range of TiO_2 have been studied, including doping with transition metals or nitrogen, and dye photosensitization [205]. While research in dye-sensitized solar electric cells have made progress towards practical implementation, dye-sensitized water photolysis cells have not produced significant yields and the materials have been unstable [99]. Such chemistries begin to resemble photosynthesis, and have been called "artificial photosynthesis" [206].

With a tandem electrode configuration of two semiconductor layers, *p*-$GaInP_2$ and GaAs, 15% solar-to-chemical (higher heating value of H_2) efficiency has been reported [207], around half the reported photovoltaic efficiency for this combination (without water splitting). A similar cell with Si and $Al_{0.15}Ga_{0.85}As$ semiconductor layers gave higher efficiency (22%, close to the reported photovoltaic efficiency) when RuO_2/Pt electrocatalysts were added [208]. An alternative PEC cell may be formed by suspending the semiconductor as tiny particles in solution and optionally loading the particles with catalysts [205,209]. However, in such a powder suspension, the produced H_2 and O_2 gasses more easily recombine than in the electrode based system, because the H_2 and O_2 production sites are located so close to each other [205].

Photoelectrochemical processes that form organic compounds from aqueous CO_2 have also been studied [210,211]. As with their hydrogen-only analogues, much work needs to be done in developing stable materials that match solar collection band gaps to electrochemical reduction energies. TiO_2 has also been examined for photolysis of CO_2 [212,213]. TiO_2 nanotubes with Pt and Cu catalysts were reported to have a factor of 20 rate increase for CH_4 production than without the Pt and Cu catalysts [214]. However, in that study the CH_4 yield was only 32 nmol/cm^2/h, equivalent to $\sim$0.01% solar-to-chemical conversion efficiency, and the CH_4 was only present as a trace gas constituent at the ppm level. CO_2 may also be supplied to non-aqueous electrolytes, which offer higher CO_2 solubility as well as an environment for potentially improved semiconductor material stability compared with water-containing systems [215].

For photoelectrolysis cells, no single material has been found that satisfies the stringent constraints [204]. The tandem semiconductor configurations are too expensive for commercial PV and may be too expensive for photoelectrochemical water splitting cells as well. The catalysts are expensive, just as they are for fuel cells and electrolysis cells. Also, long-term stability in aqueous electrolyte is uncertain. Even if a material that fulfills all of the requirements is found, it is unclear whether integrating devices into a single photoelectrochemical cell simplifies the process. With a single device, the H_2O and CO_2 must be brought to the sunlight, whereas with two devices the electrons from the PV must be transported to the electrolyzer. As mentioned above, the efficiencies that have been obtained with expensive materials are not better than what can be obtained using a PV cell powering an electrolysis cell. Photoelectrolysis of H_2O and/or CO_2 needs significant breakthroughs to become a feasible method of dissociation. At present, PV coupled to electrolysis is a more appropriate technology for solar hydrogen production than photoelectrolysis [216].

2.3. Catalytic fuel synthesis

Some of the dissociation processes produce hydrocarbons directly, but in most cases it is simpler and often beneficial to produce one or both components (CO/H_2) of syngas and catalyze fuel synthesis from these energy-rich precursors. Fischer–Tropsch synthesis (FTS) was developed in the 1920s and has been used economically as part of coal-to-liquids (CTL) and natural gas-to-liquids (GTL) projects [217]. The reaction can be represented by:

$$2H_2(g) + CO(g) \rightarrow -CH_2-(l) + H_2O(g) + 165\ kJ_{(at 400\,K)} [218]$$

where $-CH_2-$ is part of a hydrocarbon chain. A variety of hydrocarbons can be produced; chain growth depends on the

catalyst, syngas composition, and reactor temperature and pressure. High-temperature (300–350 °C) yields gasoline and low molecular mass olefins over Fe-based catalysts while low-temperature reactors (200–240 °C) yield diesel and high molecular mass linear waxes over Fe or Co-based catalysts. The water-gas shift reaction competes under certain conditions. Synthesis typically yields hydrocarbon chains with a distribution of chain lengths, up to gasoline- or diesel-like fuel distributions.

Methanol can be produced in a Fischer–Tropsch-like reaction. Traditional methanol synthesis is carried out by reforming fossil-derived syngas over a Cu-ZnO/Al_2O_3 catalyst [25] according to

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l) + 128\,kJ_{(at298\,K)}$$

with up to 18% CO_2 in the syngas. High methanol selectivity requires high pressures and low temperatures. The same catalyst can be used for methanol synthesis from CO_2 and H_2, according to

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(g) + 87\,kJ_{(at298\,K)} [25],$$

It has been stated that this type of methanol synthesis reactor (not necessarily with this particular catalyst) is commercially available with operating parameters of 50–100 bar and 200–300 °C [17]. Modified catalysts, such as those with ZrO_2-modified Al_2O_3 supports, show improvements by enhancing the dispersion of the copper particles [210,219]. Zeolite membrane reactors also show promising results [220]. It has been shown that the carbon source in such methanol synthesis is exclusively CO_2 and therefore the reaction mechanism involves hydrogenation of the adsorbed CO_2, which proceed through an intermediate species of formate ($HCOO^-$) [221]. Methanol synthesis by CO_2 hydrogenation was demonstrated as early as 1927 [222]. Many proposed CO_2-derived fuel cycles include methanol synthesis by CO_2 hydrogenation (Table 1).

Methanol-to-gasoline reactors that reform the methanol product to higher hydrocarbons have been investigated. They exhibit varying selectivity, over zeolite catalysts [25] or H-Fe silicate catalysts [210]. Methanol synthesis and reformation to gasoline have been combined in single-step CO_2 hydrogenation reactors with varying selectivities using similar Fe-based catalysts [210]. The operating conditions for these various reactors range from around 220–300 °C and 10–100 atm.

Alternative catalysts, such as Al_2O_3-supported Ni or TiO_2-supported Ru [210], instead favor the methanation of CO_2. CO_2 methanation, also known as the Sabatier process, is an exothermic reaction usually performed at temperatures of 300–400 °C that proceeds according to

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(g) + 165\,kJ_{(at298\,K)}.$$

A variety of other catalysts [210,223,224] selectively promote CO production via the reverse water-gas shift reaction (RWGS),

$$CO_2(g) + H_2(g) + 41\,kJ_{(at298\,K)} \rightarrow CO(g) + H_2O(g).$$

However, unlike the other CO_2 hydrogenation reactions, this reaction is endothermic and spontaneously yields essentially full conversion at high temperatures exceeding approximately 830 °C (see Fig. 4), at atmospheric pressure. A methanol synthesis process has been developed in which a RWGS reactor is paired with a conventional methanol synthesis reactor [225]. Similarly, producing hydrocarbons by a single-step direct hydrogenation is an active field of research [226–230]:

$$CO_2(g) + 3H_2(g) \rightarrow -CH_2-(l) + 2H_2O(g) + 125\,kJ_{(at400\,K)} [218].$$

This reaction would be advantageous since it is less exothermic than the Fischer–Tropsch reaction (this is further discussed in Section 3.1).

Finally, processes that perform fuel synthesis involving reactants other than just CO_2/CO/H_2O/H_2 have been proposed. One is the hydrogenation of $CaCO_3$ to yield hydrocarbons while regenerating $Ca(OH)_2$ as an air capture absorbent [8]. Another is a hydrothermal process that uses Fe as a reducing agent with CO_2 in an elevated-temperature aqueous system (e.g. near hydrothermal vents in the ocean) to directly yield CH_4 [231]. This is similar to a thermochemical cycle in that the oxidized Fe must be regenerated.

3. A promising pathway based on electrolysis in solid oxide cells

3.1. Process and energy balance

Of the CO_2 air capture technologies reviewed, the solid adsorbent and humidity swing method appears to have the lowest energy demand (Section 2.1). Thermal regeneration methods could also be feasible if heat management is carefully integrated with the rest of the fuel production process, but at present the energy demand and need for moving a lot of materials render these methods less economical. Electrolytic regeneration with byproduct H_2 production may become feasible with further developments of the electrolytic cell. We choose the humidity swing method for this study.

Of the dissociation technologies reviewed, high temperature electrolysis using solid oxide cells appears to be one of the most promising (Section 2.2.3.2). Recent developments and performance improvements have brought solid oxide electrolysis cells close to practical implementation. Efficient co-electrolysis of H_2O and CO_2 has been demonstrated with low cell degradation rates [36,37,182]. By supplying the proper ratio of H_2O and CO_2, syngas can be produced with a composition tailored for catalytic fuel synthesis. Despite the potential heat management complexity and the as yet unproven durability at very high current densities discussed at the end of Section 2.2.3.2, we choose the solid oxide electrolyzer over other means of dissociation. This is not to say that other means of dissociation are not worthwhile. However, critical aspects of the feasibility of heat and light driven processes have not been sufficiently demonstrated (Sections 2.2.1, 2.2.2, and 2.2.4), and because of the inherently more limited current densities of alkaline electrolyzers their capital cost is at present too expensive for intermittent operation (Section 2.2.3.1). A pathway based on capture of CO_2 from the atmosphere, high-temperature co-electrolysis of H_2O and CO_2, and Fischer–Tropsch synthesis is therefore chosen for the following analysis.

Weimer et al first proposed the use of solid oxide cells for a CO_2-recycled synthetic fuel cycle [17,18]. The proposed process used a KOH absorbent to capture CO_2 from the air, regenerated the resulting K_2CO_3 to KOH (releasing CO_2) by reacting with CaO and H_2O, and calcining the resulting $CaCO_3$ in a thermal absorbent regeneration process. Steam and the captured CO_2 are supplied together to a solid oxide cell stack for co-electrolysis, yielding syngas. The syngas is sent to a catalytic methanol synthesis reactor for methanol production. The fuel synthesis is exothermic and the authors note that the waste heat can be used to heat water to produce steam.

Here is proposed a similar process along with the energy balance, economic estimate, and discussion about implementing the process, using published experimental data when possible. The differences are the use of a new type of CO_2 air capture process which uses far less energy and costs less [1], the use of today's state-of-the-art solid oxide cells for co-electrolysis, and the use of conventional Fischer–Tropsch synthesis. Isothermal operation of the cells can be attained just above the thermoneutral voltage, taking into account small heat exchange losses as the hot outlet gasses are used to preheat the inlet gasses. Therefore the cells

Table 2
Energy balance for the process shown in Fig. 6. Units of the Q terms are kJ electricity per mol $–CH_2–$ and kJ heat per mol $–CH_2–$ for Q_{el} and Q_{th} respectively. η_{HX} is the heat exchange efficiency.

Stage	Reaction	Input				Output		
		η_{HX}	Q_{el}	Q_{th}	T (°C)	Q_{th}	T (°C)	Fuel
CO_2 air capture	CO_2 (atmosphere) → CO_2 (concentrated)		50		45		45	
H_2O desalination	2 H_2O (l, seawater) → $2H_2O$ (l, pure)		0.1		20		20	
$CO_2 + H_2O$ pre-heating	CO_2 (g) + $2H_2O$ (l) → CO_2 (g) + $2H_2O$ (g)	93%		121	20		250	
Electrolysis system[a]	$2H_2O$ (g) + CO_2 (g) → $2H_2$ (g) + CO (g) + $1.5O_2$ (g)	93%	838		250		50	
Syngas compression	$(2H_2 + CO)$ (g, 1 bar) → $(2H_2 + CO)$ (g, 20 bar)		30		50		300	
Fischer–Tropsch	$2H_2$ (g) + CO (g) → $–CH_2–$ (l) + H_2O (l)				300	209	20	647
Auxiliary components			10					
Total			928					647

[a] The electrolysis system includes the cell stack which operates at 850 °C, an ohmic heater for operating the cell below the thermoneutral voltage, a heat exchanger which heats the inlet gasses to 850 °C and cools the outlet gasses to just above the temperature of the inlet gasses, and a condenser which cools the product gasses to 50 °C and collects unconverted water.

would operate at slightly lower than the 100% operating efficiency of an electrolysis cell that was mentioned in Section 2.2.3.

The initial internal resistance of the cell stack is assumed to be 0.3 Ω cm^2 at 850 °C based on single-cell results [36,37] and assuming some additional ohmic losses from the stack interconnects. Although the cells can be run at more than −1.5 A/cm^2 at the thermoneutral voltage based on this area-specific resistance,[7] an initial current density of −0.5 A/cm^2 is assumed to minimize cell degradation, which can occur at high current densities [37,183]. Therefore the remaining heat needed is supplied by electrical heating very close to the cells; summing the internal Joule heating and this additional electrical heating, a voltage corresponding to the thermoneutral voltage plus 8% (to accommodate heat exchange losses) is supplied in total. Cell performance has been observed to degrade at a rate of 0.003 mV/h or lower for co-electrolysis operated at a fixed −0.25 A/cm^2 [36,37,182] – we assume this same degradation rate can be achieved when operated at the higher current density of −0.5 A/cm^2 assumed above. The cell stack is assumed to operate with a high $CO_2 + H_2O$ conversion (reactant utilization), which should give a composition sufficiently rich in CO + H_2 for Fischer Tropsch synthesis. The ability to operate efficiently at >90% conversion has been demonstrated [232], but no long-term durability tests have been reported. Overall, the assumptions are closely based on today's reported solid oxide cell technology with reasonable minor improvements.

Fig. 6 shows a simplified process diagram and Table 2 presents an energy balance estimate based on the assumptions. From the energy balance, electrolysis is clearly the major energy-consuming step and therefore electricity is expected to dominate the operating cost. FTS is exothermic, putting out waste heat and steam, both of which are not well utilized in existing fossil-to-liquids synthetic fuel processes [233]. However, in this process, the low-grade heat is enough to preheat the CO_2 and H_2O (to make steam) to 250 °C for the electrolyzer. This lowers the thermoneutral voltage to 1.35 V and increases the net system efficiency. The voltage applied to the cell and resistive heater is slightly higher to compensate for the assumed heat exchanger efficiency of 93%: 1.35 V/93% = 1.45 V. The higher heating value of $–CH_2–$ is 647 kJ/mol. Assuming the process is entirely driven by electricity and the waste heat is utilized as described, the total electrical energy input would be 928 kJ/mol (Table 2) and the net electricity-to-fuel efficiency would be about 70%. This is approximately double the efficiency estimated for a low temperature electrochemical process which does not include CO_2 capture nor liquid hydrocarbon fuel synthesis (it yields a gaseous mixture of CH_4, H_2, C_2H_4 and CO) [121].

Heat losses are almost entirely due to the excess heat resulting from Fischer–Tropsch synthesis. Less exothermic fuel synthesis would improve the net efficiency. As described in Section 2.3, hydrocarbon or methanol synthesis from CO_2 and H_2, instead of CO and H_2, is less exothermic. If this type of synthesis matures and proves to be efficient, it may therefore be preferable, which would make steam electrolysis preferable over co-electrolysis for this process. Another option to possibly improve the net efficiency is integrating fuel synthesis with the cell or into the outlet of the cell [30,234]. While this may simplify heat management, to fully realize the benefits of this would also require the development of cells that run in the same temperature range as fuel synthesis – then the heat generated in fuel synthesis reactions would contribute to heating the cell, resulting in minimal heat loss, in theory. The typical materials used for solid oxide electrolysis cells would not be adequate for such low temperature operation, in terms of the electrolyte conductivity and the catalytic activity of the electrodes; new materials would be needed. Alternatively, advanced alkaline water electrolysis cells could be operated at an elevated temperature that provides conditions for catalytic fuel synthesis by CO_2 hydrogenation, and CO_2 could be injected into the cathode compartment where H_2 is being produced (as mentioned near the end of Section 2.2.3.1).

If the process is driven by an intermittent power source, the efficiency will likely be somewhat lower. For example, if the electrolyzer is driven by solar power, the cells must either be heated up and cooled down each day (thermal cycling) or kept hot throughout the night, and they should be kept hot during power supply interruptions (e.g. due to clouds). This extra heating uses energy, lowering net efficiency. However, preliminary analysis of the heat management energy consumption for a well-insulated cell stack indicates that the impact on the net efficiency may be

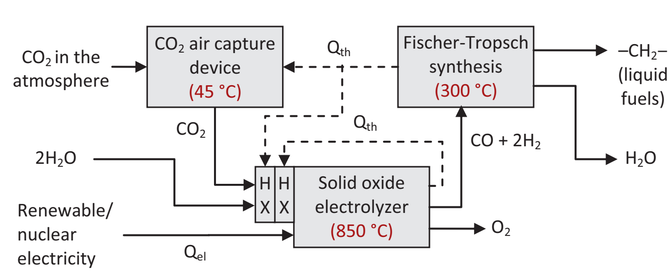


Fig. 6. Schematic of the proposed CO_2-recycled synthetic fuel production process. $–CH_2–$ represents a hydrocarbon, which could also be represented as a longer chain molecule such as C_8H_{18}. HX: heat exchanger.

[7] Assuming a reactant stream composed of >90% reactants with H_2O/CO_2 = 2 to yield the proper syngas ratio for Fischer-Tropsch and the remaining 1–10% as recycled syngas, the OCV is 0.7–0.8 V. Since the reactants are preheated by the exothermic Fischer-Tropsch reaction, the thermoneutral voltage in this case is between the steam electrolysis thermoneutral voltage (1.29 V) and that of CO_2 electrolysis (1.47 V). See references [36] and [37] for a polarization curve that illustrates this.

Table 3
Assumptions for cost estimate (also see Table 2 for assumed electricity consumption).

Cost of CO_2 capture	\$ 30/tCO_2 [1] and [see Section 2.1], broken down into 0.32 kWh/kg CO_2 electricity and \$ 15/tCO_2 capital cost based on [1]
Cost of H_2O	\$ 1 m^{-3} [see Section 2.1]
Cost of fuel synthesis	\$ 1.50/GJ Fischer–Tropsch gasoline or diesel from syngas[a] [217,233]
Cost of dissociation	
Operating temperature	850 °C
Electrolysis cell stack	\$ 2000 m^{-2} investment including financing[b]
Stack life	5 years
Balance of system	\$ 5000 m^{-2} investment including financing[b]
Balance of system life	20 years
Initial current density	-0.50 A/cm^2
Initial stack ASR	0.30 Ω cm^2
Average degradation rate	0.006 mΩ cm^2/h (based on galvanostatic degradation rates [36,37])
Capacity factor	100% = 1 − intermittency
Operating and maintenance	\$ 0.5/GJ fuel[c]

[a] Fischer–Tropsch diesel has been estimated as economically competitive when crude oil is at around \$ 20/barrel [233]. The cost of synthetic gasoline production by FT is similar, although the process is more complex [217]. This includes the cost of natural gas and reforming it to syngas, which typically accounts for 60–70% of the capital and running costs of the total plant [217]. With 6.1 GJ/barrel oil equivalent, this gives somewhat less than \$ 1.50/GJ for producing fuel from syngas; therefore \$ 1.50/GJ is a conservative estimate. Similar estimates have been made for methanol synthesis [242,243].

[b] This falls within the range of estimates for the cost of manufacturing in large-scale mass production and installing the stack and system [31,202,203,244]. Note that the stack life is shorter than the system life, so stacks will be replaced several times during the operating life of the system.

[c] This operating and maintenance cost corresponds to around 10% of the installed capital cost, which is in a similar range as or larger than O&M cost estimates for relevant industrial plants such as coal and natural gas based liquid fuel production [245,246], but lower than estimates for large alkaline electrolysis plants [97,247]. The level of automation of the facility will likely have a large impact on the O&M cost.

minor. In this analysis, these additional energy expenditures are encompassed in the "auxiliary components" in the energy balance (Table 2).

The degradation rate we assumed may in fact be lower because there may be fewer impurities in the gas stream which contribute to the degradation [182,188]. CO_2-recycled fuels will also have higher purity (e.g. without sulfur contaminants) than fossil- or biomass-derived fuels.

On the other hand, cell performance may degrade more quickly, if driven by an intermittent power source – the long-term durability of cells has not yet been extensively tested with such a degree of start-stop operation of applied voltage. If thermal cycling is necessary, degradation may be faster [235]. However, this depends on the cell; some studies have observed only minor degradation through tens of thermal cycles [160,198,235].

If a high-pressure electrolysis cell is developed, the syngas compression step can be replaced with an electrolysis-stage $H_2O + CO_2$ compression step (in addition to potential improvements in the cell current density, as has been demonstrated for low temperature electrolyzers – see Section 2.2.3.1).

No energy credit (and in the next section, no economic credit) is given for the high-purity byproduct O_2 generated at the anode during electrolysis.

Overall, the analysis presented here is simplified and requires more investigation into operation parameters and heat management strategies before implementation. However, it is useful to estimate the energy balance and economics.

3.2. Economics and implementation

Based on the above energy balance and the assumptions of Table 3, the cost of the process is estimated in Fig. 7a. The cost estimate assumes mass production of the components. It shows that synthetic gasoline could be produced by this process at U.S.D\$ 2/gal (\$ 0.53/L or \$ 15/GJ), a price competitive with the current wholesale price of conventional gasoline, if electricity costs \$ 0.02/kWh. The cost of producing synthetic diesel would be similar. It is clear that electricity makes up the majority of the total cost. This supports running the electrolysis cells as near 100% efficiency as possible, as we have assumed. However, the electrolysis capital cost depends on the current, the degradation rate, the cell lifetime, and the intermittency with which the cell is used (see Section 2.2.3), all of which are uncertainties since the technology is not fully mature and operation has not been fully optimized. If the cell stack is driven solely by a solar electricity source it will only be used about 20% of the time, which will increase the capital cost by a factor of five[8] assuming that the lifetime of the cell stack is not extended by only operating it part of the time.

The sensitivity of the fuel production cost to intermittent operation of the electrolyzer is examined in Fig. 7b, which uses the same assumptions as before but with a capacity factor of 20%. The capital cost has increased so much that even if the electricity was free, economically competitive fuels cannot be produced. In fact, commercial alkaline electrolyzers could be used at nearly the same cost in this case. However, as discussed earlier, solid oxide electrolysis cells can easily run at a higher current density without impacting the efficiency; we limited the current density to prevent degradation. If we instead assume that the cell stack could be run at -2 A/cm^2, the approximate full current density attainable at 1.45 V, with a degradation rate only three times higher than was assumed at -0.5 A/cm^2, then fuel production at U.S.D\$ 2/gal becomes feasible with highly intermittent operation, with an electricity price of 2 U.S. cents/kWh (Fig. 7d). At constant operation the electrolyzer capital cost becomes almost negligible, enabling competitive fuel production using electricity priced at 3 U.S. cents/kWh (Fig. 7c). Alternatively, the same fuel production costs can be attained by operating at a more modest -1 A/cm^2 with the same 5-year stack lifetime and driving the investment cost down to half.

Another uncertainty which must be considered is the cost of capturing CO_2 from the atmosphere. For every \$ 10/tCO_2 increase in the cost of CO_2 capture, the cost of the fuel produced will increase by 6 U.S. cents/gal (2 cents/L or \$ 0.45/GJ). While the fuel production price is less sensitive to the cost of air capture than to the electricity cost, it is not insignificant.

From this simple analysis several conclusions can be made about the process:

- With a constant power supply, synthetic gasoline can be produced at around \$ 2/gal (\$ 0.53/L) only if the electricity

[8] The CO_2 capture and fuel synthesis costs may not be affected much because they could still be operated continually by using buffers for the electricity and gasses. Since these stages consume relatively little energy the total cost should not be significantly affected by including a small electricity storage system (which could even be some of the produced syngas or synthetic fuel, e.g. using some of the solid oxide cells reversibly as fuel cells to produce electricity) and gas storage reservoirs for the CO_2 and if needed, syngas.

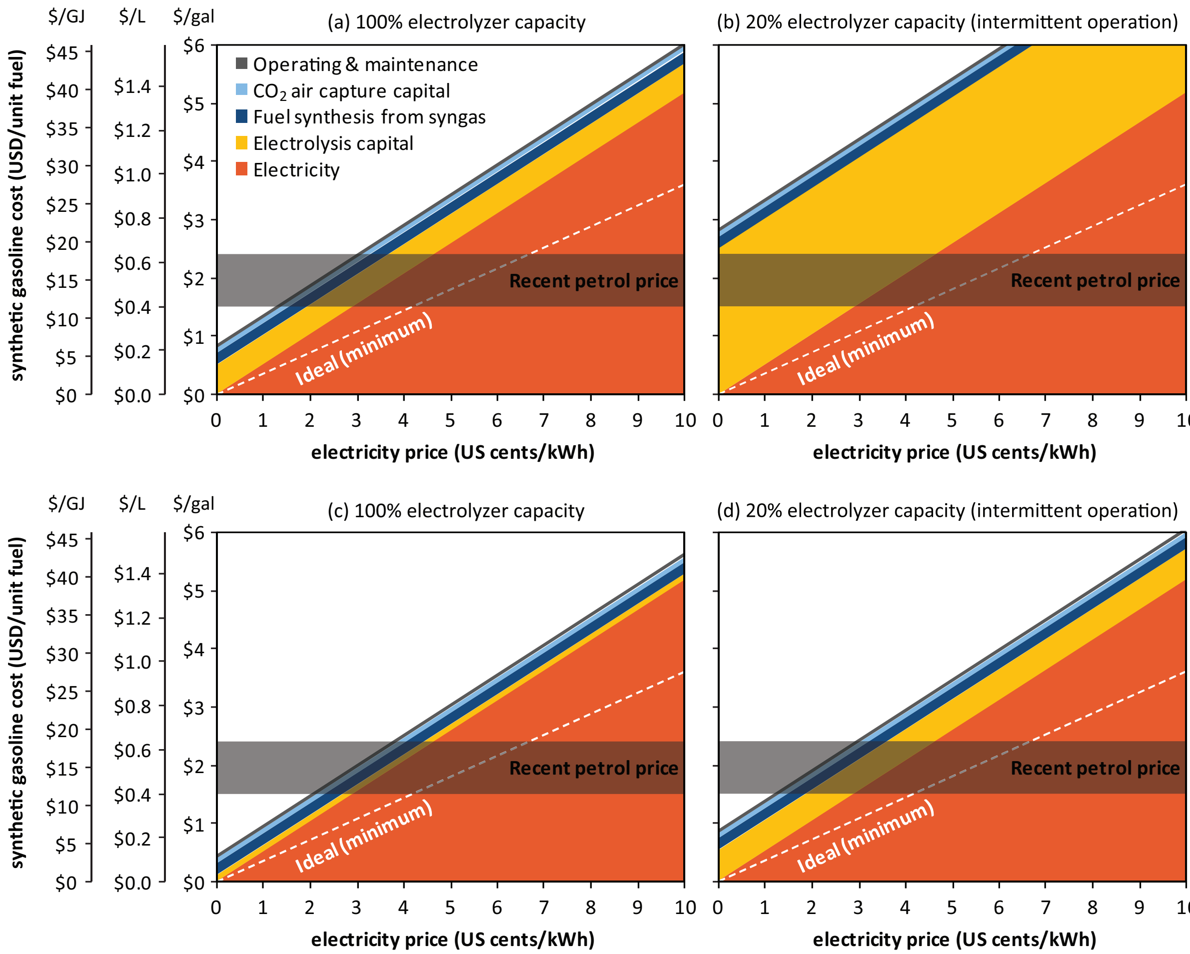


Fig. 7. Estimate of synthetic fuel cost versus electricity price using (a) the assumptions of Table 3 including constant operation, (b) the same assumptions but with highly intermittent operation (a 20% capacity factor), and operating the electrolyzer at a higher current density with (c) constant operation and (d) highly intermittent operation. See discussion in the text about the higher current density scenario.

price is less than 3 U.S. cents/kWh. This is true for the base case of the electrolyzer technology and in case of significant technology improvements (even if the electrolyzer had zero capital cost). If a higher gasoline price of $ 3/gal ($ 0.78/L) is competitive, the price of electricity driving the synthetic fuel process must be 4–5 U.S. cents/kWh, which is a similar range to recent average wholesale electricity prices in the U.S.

- Regarding the capital cost, intermittency is a very important factor which deserves a more detailed economic analysis. Without intermittency, electricity – not the electrolyzer capital cost – dominates the cost of fuel production. However, with intermittent power, economical fuel production using 2 U.S. cents/kWh electricity will depend on some improvements in electrolyzer technology – greater durability in high current density operation and/or lower investment cost. Optimizing cells to maintain durable performance while operating at the high current density attainable at the thermoneutral voltage is a straightforward way to reduce the capital cost. Reducing the investment cost may require focus on the balance of system components since these components may dominate the investment cost [202,203].
- Fuel synthesis and CO_2 air capture are stages that would not be present for a hydrogen fuel cycle. The hydrogen fuel cycle would instead have a high cost of distribution since a new infrastructure would need to be built. In the CO_2-recycled fuel production process, the net cost of fuel synthesis and CO_2 air capture together is at most $ 6/GJ fuel (based on an capture cost of $ 100/tCO_2, which is on the high end of estimates for air capture [49]). A hydrogen distribution infrastructure including filling stations has been estimated to cost at least this much if not several times more [236,237] depending on the level of market penetration. These costs would come in the form of massive capital investments which would demand immediate widespread adoption of hydrogen fueled vehicles in order to be economical. CO_2-recycled hydrocarbon fuels, on the other hand, can smoothly substitute into the existing hydrocarbon fuel infrastructure and scale up naturally as the market demands.

From an economic standpoint, the process should always be run with a constant-supply power source because constant operation lowers the capital cost. Therefore, hydroelectric, geothermal, or nuclear power would be preferable. Iceland appears to be in a unique position, as mentioned in Section 2.1. Iceland has an abundance of inexpensive geothermal and hydroelectric energy. Due to Iceland's isolated location the country cannot export this energy directly as electricity. The country exports this energy embedded in products like aluminum. Producing synthetic hydrocarbon fuels by this method would be another, potentially extremely valuable, avenue to exporting this low cost renewable energy.

In most cases, though, excess constant-supply power is not available. Synthetic fuel production will compete with other electricity consumers for a time-varying supply of electricity. Since synthetic fuel production does not *need* electricity on demand, it could take advantage of intermittent electricity sources which do not work well on the power grid. Storage of intermittent renewable energy as synthetic fuels could be an advantageous way to get that renewable energy to the consumer, as mentioned in Section 1.

The most advantageous intermittent electricity sources would be those that are situated in ideal locations for energy collection, which can include remote locations far from existing electricity grid infrastructure. Solar power in a sunny desert is one such scenario that can provide cheap intermittent electricity. Solar insolation can be several times higher in the desert than in areas that need fuel. Therefore, a renewable electricity source that is currently too expensive to situate near the electric grid to provide grid electricity might be used in a remote location to economically produce high value fuels. Furthermore, PV deployment in non-grid applications can benefit the cost learning-curve for PV cells [238], accelerating the cost reductions necessary for PV to become competitive in the grid. If the synthetic fuel technology were to be implemented in the dry desert, water supply might be a concern. However, the water needed for electrolysis and other components of the process could simply be transported to the site by the same means that the fuel product would be transported away from the site. The volume of water required for producing the hydrogen embedded in fuel only slightly exceeds the amount of fuel produced.

Solid oxide electrolysis cells are also being considered for integration with wind power. Excess bursts of wind power could be very cheap, but such a power source would be highly intermittent, requiring a very inexpensive electrolysis capital cost to produce gasoline for less than U.S.D$ 2–3/gal.

On the other hand, grid-connectivity could be advantageous. Operating the solid oxide cells reversibly, as electrolysis cells when the renewable electricity is supplied and as fuel cells when consumers demand electricity, may be an advantageous method of large-scale electricity storage for managing intermittent electricity sources like solar and wind, as an alternative to (or in cooperation with) other means of storage such as in batteries or compressed air energy storage. Excess supply could be used for transportation fuel production by CO_2 recycling. In such a scenario, since the cells would be operated in fuel cell mode in addition to electrolysis mode, the capacity factor of the cells would be higher than for cells dedicated to electrolysis only, which could improve the economics.

In discussing the economics of synthetic hydrocarbons, one study concluded that "only under exceptional circumstances would one form of secondary energy (electricity) be converted to another (hydrogen)" [38]. However, one should make a clear distinction between primary electric energy and secondary electric energy. The latter is produced (e.g. from fossil fuel) in order to satisfy customer demand. The former is the result of physical constraints and it is delivered whenever the system (e.g. the photovoltaic panel or wind turbine) is ready to produce electricity. Clearly, secondary electricity is far more valuable than primary electricity. Primary electricity can be converted to whatever form of energy is more valuable than itself. So the circumstances under which electricity would be converted to fuel need not be exceptional: the value of chemical fuels need only be greater than the value of carbon-neutral electricity. Today, this is already the case in some locations. Iceland is one example, as mentioned above. In Norway, another country with an abundance of renewable energy sources, the pre-tax price of diesel fuel is about twice the pre-tax price of electricity on an energy equivalent basis[9] [239]. These are circumstances in which the CO_2-recycled fuel process might be first implemented – where economic viability is closest to being within reach. In the long term, as renewable and nuclear energy sources scale up and other countries become renewably powered like Iceland and Norway, as gas prices rise, and as the technologies involved in the CO_2 recycling process are improved, the circumstances will become more and more common and the economics of the synthetic fuel process will become more favorable.

Since CO_2-recycled synthetic fuels are environmentally friendly (potentially more so than biofuels), they might go to market without the same level of taxation as gasoline in some countries. This would give these clean fuels an advantage as they would be competing against the post-tax price of gasoline rather than the wholesale price. A price on CO_2 emissions would likely further improve the economic competitiveness of CO_2-based synthetic fuels. Finally, the potentially greater sustainability of CO_2-recycled fuels over fossil or biomass derived fuels, as well as independence from the geographic and supply related issues of conventional fuels, could also give CO_2-recycled fuels a market advantage.

4. Conclusion

This article has reviewed and analyzed numerous ways sustainable hydrocarbon fuels could be produced from CO_2, H_2O, and renewable and/or nuclear energy. A process to produce such fuels has three stages: (1) CO_2 capture, (2) storage of the renewable or nuclear energy as chemical energy by dissociation of CO_2 and/or H_2O, and (3) fuel synthesis using the dissociation products. Combining more than one stage into a single unit is possible, but there may be benefits to optimizing each stage separately. The status of the enabling technologies for each stage was examined, with special focus on the various thermochemical, electrochemical and photochemical energy conversion technologies that could be used for dissociation of H_2O and CO_2, the stage with the highest energy consumption. Capturing CO_2 from the atmosphere using a solid sorbent, electrolyzing H_2O and CO_2 in high temperature solid oxide cells to yield a mixture of H_2 and CO (syngas), and producing gasoline or diesel from the syngas in a catalytic reactor (e.g. Fischer–Tropsch) was identified as one of the most promising, feasible routes and analyzed further in terms of energy balance and economics.

Based on the energy balance and economics estimates presented for this particular co-electrolysis based cycle, the state-of-the-art technologies at each stage of the cycle can be combined to work together efficiently today with an electricity-to-liquid fuel conversion efficiency of about 70%, and with mass production of the components, economic viability is feasible. With an electricity price of less than 3 U.S. cents/kWh from a constant power supply (e.g. geothermal, hydroelectric, or nuclear), the synthetic fuel price could be competitive with gasoline at around U.S.D$ 2/gal ($ 0.53/L). If a higher gasoline price of $ 3/gal ($ 0.78/L) is competitive, the price of electricity driving the synthetic fuel process must be 4–5 U.S. cents/kWh, which is a similar range to recent average wholesale electricity prices in the U.S. Intermittent power sources would significantly increase the capital cost of the

[9] Regarding the use of pre-tax prices: Although the end-user post-taxation price of liquid fuels is higher than that of electricity in most parts of the world, liquid fuels are more heavily taxed than electricity, so one must compare the pre-tax prices [239]. Regarding energy equivalence: $ 0.03/kWh is equivalent to $ 1.10/gal or $ 0.29/L gasoline based on an energy density of 34.5 MJ/L gasoline. Energy-equivalent prices are based on an ideal energy conversion – if one could simply turn electrical energy into hydrocarbon fuel without paying anything (energy, equipment, etc.) for the conversion. Based on the cost estimates shown in Fig. 7, one can see that the conversion might add from $ 0.45/gal to $ 2.85/gal ($ 0.12–0.75/L) depending on the technologies.

electrolyzer. With intermittent operation, economical fuel production most likely requires additional technology development on the electrolysis system to reduce the capital cost (via achieving durable high current density operation and/or lower manufacturing cost). Several developments could enable competitive fuel production using any inexpensive sustainable power sources:

- Further development of the CO_2 air capture process and full-scale demonstration, followed by cost reductions from mass production. In the near term, however, CO_2 collected from industrial sources rather than the atmosphere could be used in the non-closed-loop version of the synthetic fuel process.
- Demonstration of durable operation of solid oxide electrolysis cell stacks at high current densities ($\geq$1 A/cm^2). Since the existing cells can be efficiently operated at such high current densities at the thermoneutral voltage, operating at this point would be a straightforward way to improve the economics, if performance at this operating point can be maintained over long-term operation.
- Demonstration of intermittent cell operation, which may require development of specialized power management and heat management schemes.

Circumstances for initial implementation were discussed. Sites with excess inexpensive constant-supply renewable power, such as those available in Iceland, are ideal. However, since these circumstances are rare, large-scale implementation depends on using inexpensive, intermittent renewable energy (e.g. solar arrays built in remote, sunny locations such as the desert, or excess wind power supply) and/or constant-supply nuclear power for synthetic fuel production.

With feasible technology development and mass production of the process components, CO_2-recycled hydrocarbon fuels can be produced at the scale needed to replace transportation fuels at a price competitive with more conventional fossil-derived hydrocarbons, especially if oil and CO_2 sequestration costs are high. The potentially greater sustainability of CO_2-recycled fuels over fossil or biomass derived fuels, as well as independence from the geographic and supply related issues of conventional fuels, could also give CO_2-recycled fuels a market advantage.

Acknowledgements

Financial support from the American Chemical Society Petroleum Research Fund, the Lenfest Center for Sustainable Energy, and from the Programme Commission on Sustainable Energy and Environment, The Danish Council for Strategic Research, via the SERC project (www.serc.dk), is gratefully acknowledged.

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